Asymmetric Pyrone Diels–Alder Reactions Enabled by Dienamine Catalysis

Charles J. F. Cole, Lilia Fuentes, and Scott A. Snyder*

Department of Chemistry, The University of Chicago, 5735 S. Ellis Avenue, Chicago, IL 60637 (USA)

Supporting Information Section

Table of Contents

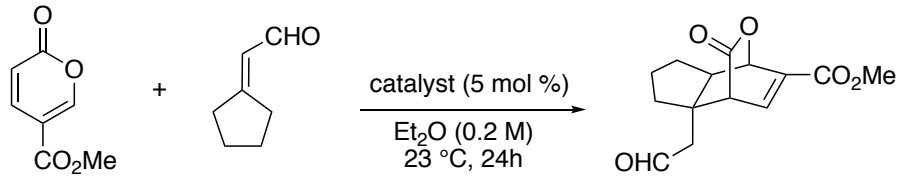
Experimental Data for Compounds

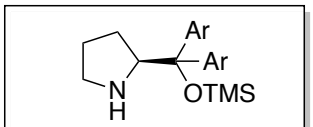
A. General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, diethyl ether (Et_2O) dichloromethane (CH_2Cl_2), and acetonitrile (CH_3CN) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent, and an ethanolic solution of phosphomolybdic acid and cerium sulfate or a solution of $KMnO_4$ in aq. $NaHCO_3$ and heat as developing agents. SiliCycle silica gel (60, academic grade, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker 400 and 500 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, app = apparent. IR spectra were recorded on a Perkin-Elmer 1000 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on Agilent 6244 Tof-MS using ESI (Electrospray Ionization) at the University of Chicago Mass Spectroscopy Core Facility. All *ee* values were determined by HPLC on Daicel Chiralcel or Chiralpak columns in comparison with racemic samples.

B. Abbreviations. EtOAc = ethyl acetate, PCC = pyridinium chlorochromate, AcOH = acetic acid, 4-DMAP = 4-*N,N*-dimethylaminopyridine, Et_3N = triethylamine, *i*-PrOH = isopropanol, NaOAc = sodium acetate, AIBN = 2,2'-azobis(2-methyl propionitrile), DCE = 1,2-dichloroethane, TMSOTf = trimethylsilyl trifluoromethanesulfonate.

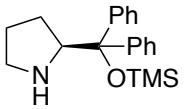
C. Screening and Optimization

Table S1. Catalyst Screening[a]

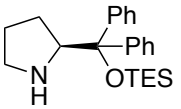




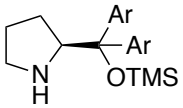
20
Ar = 3,5-$(CF_3)_2C_6H_3$
(93%, 6.7:1.0 *dr*, 95% *ee*)



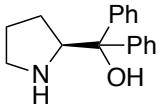
13
(70%, 2.3:1.0 *dr*, 90% *ee*)



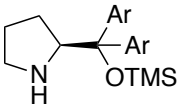
25
(64%, 3.5:1.0 *dr*, 92% *ee*)



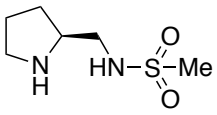
S1
Ar = 3,5-(tBu)$_2$C$_6$H$_3$
(85%, 2.0:1.0 *dr*, 80% *ee*)



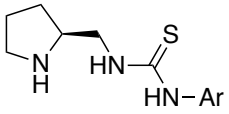
S2
(16%, 1.0:9.0 *dr*, 20% *ee*)



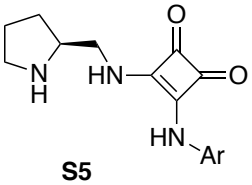
S3
Ar = 2-naphthyl
(71%, 1.0:1.0 *dr*, 70% *ee*)



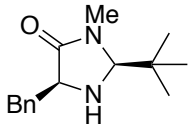
S4
[N.R.]



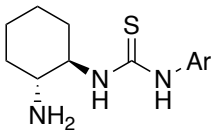
26
Ar = 3,5-$(CF_3)_2C_6H_3$
(10%, 3.0:1.0 *dr*, 20% *ee*)



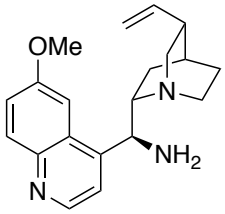
S5
Ar = 3,5-$(CF_3)_2C_6H_3$
(64%, 3.5:1.0 *dr*., 21% *ee*)



S6
[N.R.]



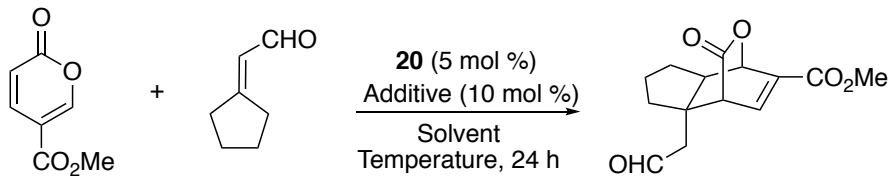
27
Ar = 3,5-$(CF_3)_2C_6H_3$
[N.R.]



S7
[N.R.]

[a] Conditions: **22** (0.3 mmol), **23** (0.9 mmol) and catalyst (0.05 mmol) were combined in a 1 dram screw capped vial, dissolved in solvent and monitored by TLC until consumption of starting material was observed. Yields represent combined isolated yields. *dr* was determined by crude ^{1}H NMR analysis and *ee* determined by HPLC analysis using a chiral stationary phase.

Table S2. Optimization of Reaction Conditions[a]

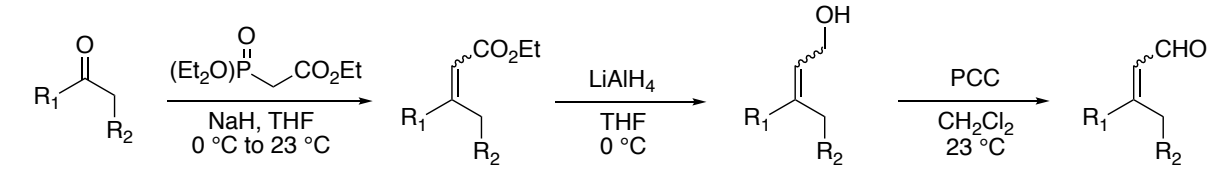


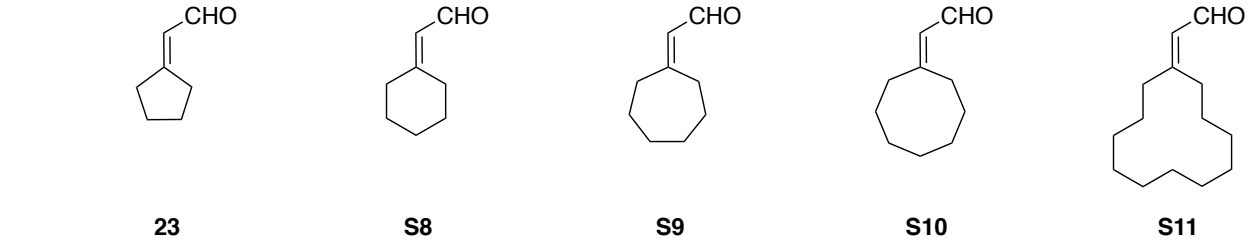
Entry	Additive	Solvent (M)	Temperature (°C)	Conc. (M)	Yield (%)[b]	*dr*[c]	*ee* (%)[d]
1	$PhCO_2H$	Et_2O	23	0.2	56	5.7 : 1.0	93
2	$PhCO_2H$[e]	Et_2O	23	0.2	37	4.6 : 1.0	87
3	$PhCO_2H$[f]	Et_2O	23	0.2	49	5.7 : 1.0	90
4	AcOH	Et_2O	23	0.2	67	1.9 : 1.0	90
5	Et_3N	Et_2O	23	0.2	13	4.9 : 1.0	n.d.
6	–	**Et_2O**	**23**	**0.2**	**93**	**6.7 : 1.0**	**94**
7	–	Et_2O	23	0.1	87	5.3 : 1.0	91
8	–	Et_2O	23	0.4	65	2.0 : 1.0	90
9	–	Et_2O	0	0.2	Trace	n.d.	n.d.
10	–	Et_2O	40	0.2	70	1.6 : 1.0	88
11	–	MeCN	23	0.2	62	1.5 : 1.0	81
12	–	Toluene	23	0.2	68	2.0 : 1.0	89
13	–	THF	23	0.2	90	1.5 : 1.0	86
14	–	CH_2Cl_2	23	0.2	69	1.2 : 1.0	83
15	–	EtOH	23	0.2	Decomp.	n.d.	n.d.

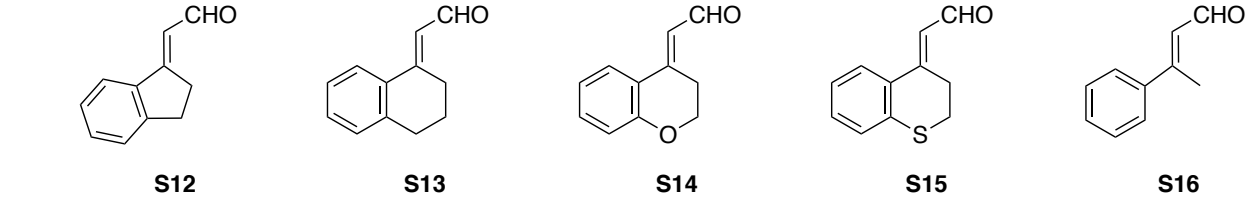
[a] Conditions: **22** (0.3 mmol), **23** (0.9 mmol), **20** (0.05 mmol) and additive (0.1 mmol) were combined in a 1 dram screw capped vial, dissolved in solvent and monitored by TLC until consumption of starting material was observed. [b] Combined isolated yield. [c] Determined by crude ^1H NMR analysis. [d] Determined by HPLC analysis usinga chiral stationary phase. [e] 20 mol % of additive. [f] 20 mol % of additive.

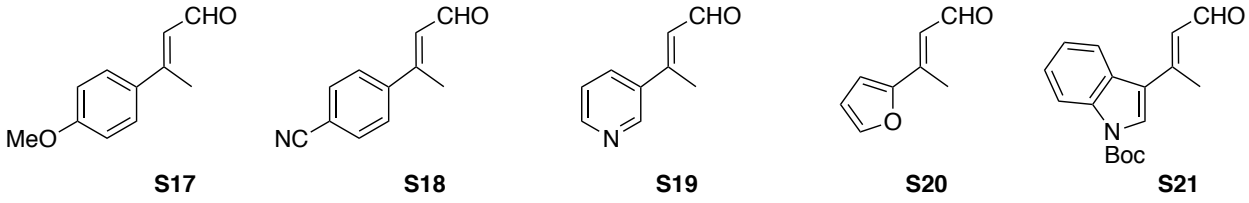
D. Preparation of Starting Materials

General Procedure A: Preparation of α,β-Unsaturated Aldehydes:[1]





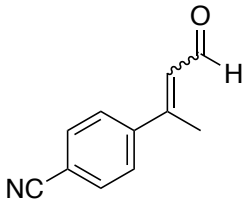




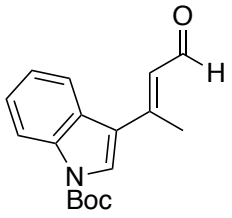
General procedure illustrated using the preparation of S16. To a dry flask containing THF (40 mL) at 23 °C was added NaH (60% dispersion in mineral oil, 1.06 g, 26.6 mmol, 1.6 equiv) and the suspension was cooled to 0 °C. To this suspension was then added triethylphosphonoacetate (4.96 mL, 25.0 mmol, 1.5 equiv) dropwise. After 15 min of stirring, a solution of acetophenone (2.00 g, 16.6 mmol, 1.0 equiv) in THF (15 mL) was added dropwise at 0 °C. The reaction solution was then warmed to 23 °C and reaction progress was monitored by TLC. Once the starting material was consumed (typically 6–8 h), the reaction contents were quenched with water (50 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (2 × 30 mL). The organic layers were then combined, dried (Na_2SO_4), and concentrated. The resultant crude residue was purified by flash column chromatography (silica gel, hexanes/EtOAc, 9:1) to give the desired α,β-unsaturated ester (2.82 g, 90% yield) as a pale yellow oil. Next, $LiAlH_4$ (0.558 g, 14.7 mmol, 1.0 equiv) was added into a dry flask and then THF (50 mL) was added at 23 °C. This suspension was then cooled to 0 °C and a solution of the α,β-unsaturated ester (2.80 g, 14.7 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. Upon completion, the reaction contents were quenched by the addition of water (0.5 mL), 0.05 M NaOH

(0.5 mL), and water (1.0 mL). The resultant mixture was filtered through Celite and concentrated to give the desired crude allylic alcohol. Pressing forward without any additional purification, the allylic alcohol (2.15 g, 14.5 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (250 mL) and PCC (4.67 g, 21.8 mmol, 1.5 equiv) was added portion-wise at 23 °C. Upon completion, the reaction mixture was filtered through Celite on top of a pad of silica gel, with the product being eluted with CH_2Cl_2 to give the desired α,β-unsaturated aldehyde (1.48 g, 70% yield) as a bright yellow oil. *Note:* In certain cases, oxidation of the allylic alcohol with PCC resulted in decomposition or a much more complex reaction mixture. Therefore, in the preparation of aldehydes **S18, S19**, **S20** and **S21**, the following procedure using MnO_2 was performed instead. The allylic alcohol (0.125 g, 1.00 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (15 mL) followed by the addition of activated MnO_2 (1.30 g, 15.0 mmol, 15 equiv). The resultant reaction mixture was stirred at 23 °C for 16 h. Upon completion, the reaction contents were filtered through Celite and concentrated. The resultant residue was further purified by flash column chromatography (silica gel, hexanes/EtOAc, 9:1) to give the desired α,β-unsaturated aldehyde (0.100 g, 80% yield) as a yellow oil.

α,β-unsaturated aldehydes **23**,[1] **S8**,[1] **S9**,[1] **S10**,[2] **S11**,[3] **S12**,[4] **S13**,[4] **S14**,[4] **S15**,[4] **S16**,[5] **S17**,[5] **S18**, **S19**,[5] **S20**,[5] and **S21** were prepared according to the above procedure and all spectra matched that previously reported. Citral (**52**) was obtained from commercial sources as a mixture of *E/Z* isomers and used without any further purification.

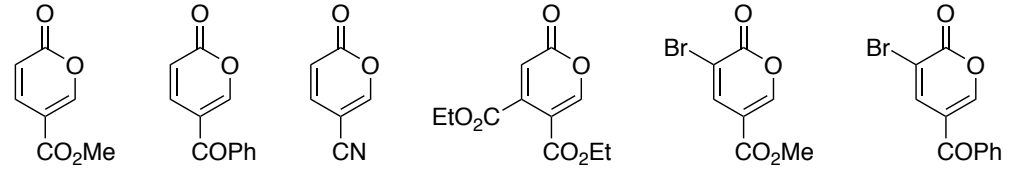


4-(4-oxobut-2-en-2-yl)benzonitrile (S18). Prepared according to the general procedure described above and characterized as a mixture of *E/Z* isomers. **S18**: R_f = 0.56 (silica gel, hexanes/EtOAc, 2:1); IR (thin film) 2956, 2229, 1725, 1669, 1142, 826 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.17 (dd, *J* = 7.8, 2.0 Hz, 1 H), 9.38 (dd, *J* = 8.1, 1.9 Hz, 1 H), 7.70 (td, *J* = 8.4, 1.9 Hz, 4 H), 7.61 (d, *J* = 8.1 Hz, 2 H), 7.41 (d, *J* = 7.9 Hz, 2 H), 6.37–6.32 (m, 1 H), 6.16 (ddd, *J* = 8.2, 2.9, 1.5 Hz, 1 H), 2.56 (d, *J* = 1.8 Hz, 3 H), 2.30 (d, *J* = 1.8 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.99, 190.78, 159.40, 154.96, 145.16, 143.13, 132.56, 132.35, 130.21, 129.01, 128.96, 126.98, 118.29, 118.17, 113.41, 112.99, 26.23, 16.39; HRMS (ESI) calcd for $C_{11}H_8N^+$ $[M + H – H_2O]^+$ 154.0651, found 154.0647.



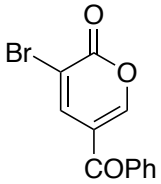
***tert*-Butyl-(*E*)-3-(4-oxobut-2-en-2-yl)-1*H*-indole-1-carboxylate (S21).** Prepared according to the general procedure described above. **S21**: R_f = 0.35 (silica gel, hexanes/EtOAc, 2:1); IR (thin film) 2980, 2933, 2828, 1737, 1662, 1452, 1371, 1151, 745 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 10.24 (d, *J* = 7.9 Hz, 1 H), 8.20 (d, *J* = 8.3 Hz, 1 H), 7.92 (s, 1 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.41–7.35 (m, 1 H), 7.31 (t, *J* = 7.8 Hz, 1 H), 6.66 (dd, *J* = 7.8, 1.5 Hz, 1 H), 2.61 (s, 3 H), 1.70 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.10, 151.08, 149.33, 136.37, 127.41, 126.90, 126.86, 125.33, 123.78, 121.96, 121.06, 115.75, 85.01, 28.27, 16.98; HRMS (ESI) calcd for $C_{17}H_{19}NO_3^+$ $[M]^+$ 285.1365, found 285.1362.

Preparation of Pyrones:



22 **S22** **S23** **S24** **S25** **S26**

Methyl coumalate (**22**) was obtained from commercial sources and used without further purification. Pyrones **S22**,[6] **S23**,[7] **S24**,[8] and **S25**[7] were prepared using previously published procedures. The preparation of **S26** is described below.

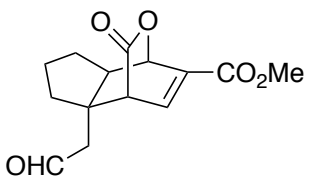


5-benzoyl-3-bromo-2*H*-pyran-2-one (S26). To a solution of pyridinium tribromide (1.25 g, 3.9 mmol, 1.3 equiv) in AcOH (3.0 mL) at 60 °C was added **22** (0.60 g, 3.0 mmol, 1.0 equiv) portionwise. The reaction mixture was heated at reflux for 1 h. Upon completion, the reaction contents were cooled to 23 °C and the excess bromine was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (5 mL) and saturated aqueous $NaHCO_3$ (5 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL) and the organic layers were combined, dried (Na_2SO_4) and concentrated. The resultant dark brown oil was further purified by flash column chromatography (silica gel, hexanes/EtOAc, 9:1) to afford the desired product (0.44 g, 53% yield) as a yellow solid. **S26**: R_f = 0.42 (silica gel, hexanes/EtOAc, 2:1); IR (thin film) 3077, 2925, 2855, 1749, 1658, 1285 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 2.3 Hz, 1 H), 8.04 (d, J = 2.3 Hz, 1 H), 7.74 (d, J = 7.5 Hz, 2 H), 7.65 (t, J = 7.4 Hz, 1 H), 7.54 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.32, 157.47, 143.11, 136.24, 133.59, 130.25, 129.30, 129.16, 119.58, 112.69; HRMS (ESI) calcd for $C_{12}H_7O_3Na_2^+$ $[M + 2Na]^+$ 161.9682, found 161.9681.

E. Dienamine Catalyzed Pyrone Diels–Alder Reaction

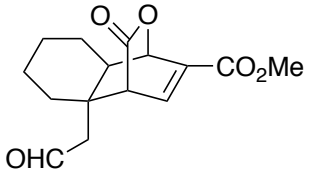
General Procedure B: Dienamine-Catalyzed [4+2]-Cycloaddition

To a 1 dram screw-capped vial was added the pyrone substrate (0.30 mmol, 1.0 equiv), (*S*)-α,α-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethylsilyl ether (9.0 mg, 0.015 mmol, 0.05 equiv), the α,β-unsaturated aldehyde (0.90 mmol, 3.0 equiv) and Et_2O (1.5 mL). The reaction contents were stirred at 23 °C for 24 h. Upon completion, the reaction mixture was subjected directly to flash column chromatography to give the desired cycloadducts. In order to determine enantiomeric excess, all aldehydes were converted into the corresponding α,β-unsaturated ester as follows: to a 1 dram screw-capped vial containing a solution of the cycloadduct (0.1 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL) at 23 °C was added methyl (triphenylphosphoranylidene)acetate (0.100 g, 0.3 mmol, 3.0 equiv) and the reaction mixture stirred at 23 °C for 1 h. Upon completion, the crude reaction mixture was subjected directly to preparative TLC (silica gel, hexanes/EtOAc, 3:1) to afford the desired product that was subsequently analyzed by HPLC.



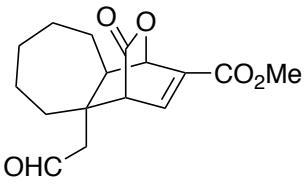
Methyl (3a*R*,4*R*,7*R*,7a*R*)-8-oxo-7a-(2-oxoethyl)-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-(epoxymethano)indene-5-carboxylate (*Endo*-24). Prepared following the general procedure described above**,** the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (73.0 mg combined, 93% combined yield; 62.3 mg, 80% yield ***Endo*-24**; 10.7 mg, 13% yield ***Exo*-24**) as a pale yellow oil. The *dr* was 6.7:1 as determined by crude ^{1}H NMR. ***Endo*-24**: R_f = 0.13 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = –6.00° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2955, 2870, 1759, 1718, 1258 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 1.8 Hz, 1 H), 7.28 (dd, *J* = 6.4, 2.1 Hz, 1 H), 5.45 (d, *J* = 1.9 Hz, 1 H), 3.80 (s, 3 H), 3.77 (d, *J* = 6.4 Hz, 1 H), 2.52 (dd, *J* = 16.7, 1.6 Hz, 1 H), 2.41 (dd, *J* = 16.6, 2.2 Hz, 1 H), 2.04–1.98 (m, 2 H), 1.88–1.74 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.94, 171.54, 162.69, 140.98, 137.55, 77.55, 53.15, 52.44, 51.40, 49.63, 48.15, 36.05, 28.57, 27.27; HRMS (ESI) calcd for $C_{14}H_{15}O_4^+$ $[M + H - H_2O]^+$ 247.0965, found: 247.0966. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 85:15, flow rate of 1.0 mL/min, 215 nm) R_t = 8.83 min (minor), R_t = 11.42 min (major), 94% *ee*.

***Exo*-24**: R_f = 0.16 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = +2.42 (*c* = 1.0 in $CHCl_3$). IR (thin film) 2955, 2872, 1759, 1718, 1258 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (t, *J* = 1.2 Hz, 1 H), 7.34 (dd, *J* = 6.6, 2.4 Hz, 1 H), 5.54 (dd, *J* = 4.3, 2.4 Hz, 1 H), 4.01 (d, *J* = 6.6 Hz, 1 H), 3.83 (s, 3 H), 2.75 (dd, *J* = 17.9, 1.4 Hz, 1 H), 2.71–2.63 (m, 1 H), 2.53 (ddd, *J* = 8.8, 7.0, 4.2 Hz, 1 H), 2.00 (dq, *J* = 13.8, 6.8 Hz, 1 H), 1.83 (dt, *J* = 12.4, 5.6 Hz, 1 H), 1.66–1.60 (m, 2 H), 1.51 (dt, *J* = 13.6, 8.2 Hz, 1 H), 1.11 (dq, *J* = 14.0, 7.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.51, 171.88, 163.34, 141.30, 136.76, 76.96, 53.42, 52.51, 52.11, 50.31, 47.72, 36.47, 28.74, 27.01; HRMS (ESI) calcd for $C_{14}H_{17}O_5^+$ $[M + H]^+$ 265.1071, found 265.1060. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 215 nm) R_t = 15.30 min (major), R_t = 19.32 min (minor), 85% *ee*.

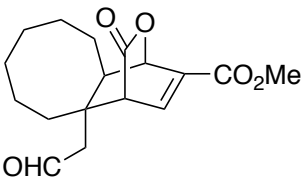


Methyl (1*R*,4*R*,4a*R*,8a*R*)-9-oxo-4a-(2-oxoethyl)-1,4,4a,5,6,7,8,8aoctahydro-1,4-(epoxymethano)naphthalene-2-carboxylate (*Endo*-28). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (41.0 mg combined, 50% combined yield; 28.7 mg, 35% yield ***Endo*-28**; 12.3 mg, 15% yield ***Exo*-28**) as a colorless oil. The *dr* was 3.1:1 as determined by crude ^{1}H NMR. ***Endo*-28**: R_f = 0.17 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –33.96° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2951, 2871, 1759, 1717, 1633, 1261 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (t, *J* = 2.2 Hz, 1 H), 7.25 (dd, *J* = 5.9, 1.7 Hz, 1 H), 5.35–5.33 (m, 1 H), 3.80 (s, 4 H), 2.57 (dd, *J* = 16.0, 2.2 Hz, 1 H), 2.11 (dt, *J* = 16.0, 2.1 Hz, 1 H), 1.89–1.73 (m, 3 H), 1.72–1.53 (m, 3 H), 1.52–1.43 (m, 1 H), 1.40–1.28 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.93, 171.38, 162.62, 139.20, 136.81, 77.33, 52.43, 51.51, 50.68, 44.20, 37.86, 27.39, 22.61, 18.69, 16.70; HRMS (ESI) calcd for $C_{15}H_{17}O_4^+$ $[M + H - H_2O]^+$ 261.1121, found 261.1123. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 19.75 min (minor), R_t = 26.89 min (major), 94% *ee*.

***Exo*-28**: R_f = 0.25 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = +7.30° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2936, 2868, 1759, 1719, 1638, 1257 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.79 (dd, *J* = 2.6, 1.1 Hz, 1 H), 7.32 (dd, *J* = 6.6, 2.3 Hz, 1 H), 5.44 (dd, *J* = 3.6, 2.2 Hz, 1 H), 3.95 (d, *J* = 6.6 Hz, 1 H), 3.81 (s, 3 H), 2.74 (dd, *J* = 17.1, 2.5 Hz, 1 H), 2.44 (dt, *J* = 17.3, 1.4 Hz, 1 H), 1.86 (ddd, *J* = 12.9, 5.3, 3.6 Hz, 1 H), 1.79–1.45 (m, 4 H), 1.37–1.22 (m, 1 H), 1.16 (dddd, *J* = 14.3, 12.9, 7.3, 1.9 Hz, 1 H), 0.71 (qd, *J* = 13.3, 3.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.55, 171.39, 163.13, 140.73, 135.03, 77.14, 52.45, 51.62, 50.87, 46.07, 38.86, 26.06, 23.24, 18.57, 16.38; HRMS (ESI) calcd for $C_{15}H_{18}O_5^+$ $[M]^+$ 278.1154, found 278.1151. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 24.05 min (major), R_t = 27.30 min (minor), 73% *ee*.



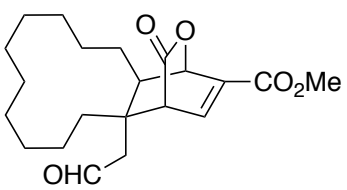
Methyl (1*R*,4*R*,4a*R*,9a*R*)-10-oxo-4a-(2-oxoethyl)-4,4a,5,6,7,8,9,9a-octahydro-1*H*-1,4-(epoxymethano)benzo[7]annulene-2-carboxylate (*Endo*-29). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (68.0 mg combined, 76% combined yield; 62.3 mg, 70 % yield ***Endo*-29**; 5.7 mg, 6% yield ***Exo*-29**) as a colorless oil. The *dr* was 8.7:1 as determined by crude ^1H NMR. ***Endo*-29**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –31.76° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2927, 2856, 1758, 1717, 1637, 1258, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.72 (d, *J* = 2.0 Hz, 1 H), 7.29 (d, *J* = 6.4 Hz, 1 H), 5.25 (d, *J* = 1.6 Hz, 1 H), 3.79 (d, *J* = 1.5 Hz, 3 H), 3.71 (dd, *J* = 6.4, 1.3 Hz, 1 H), 2.86 (dt, *J* = 16.2, 1.6 Hz, 1 H), 2.15 (dd, *J* = 16.2, 1.9 Hz, 1 H), 2.06–1.91 (m, 3 H), 1.83 (d, *J* = 13.2 Hz, 2 H), 1.76–1.65 (m, 1 H), 1.62–1.41 (m, 3 H), 1.33–1.14 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.83, 171.30, 162.70, 140.41, 136.86, 79.49, 53.51, 52.39, 51.70, 49.46, 42.13, 34.42, 31.17, 30.66, 28.21, 24.76; HRMS (ESI) calcd for $C_{16}H_{21}O_5^+$ $[M + H]^+$ 293.1384, found 293.1392. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 19.49 min (minor), R_t = 28.49 min (major), 97% *ee*.



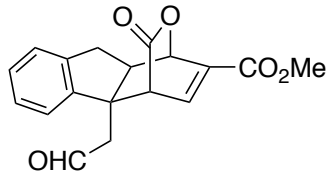
2-((1*R*,4*R*,4a*R*,10a*R*)-2-((methylperoxy)methyl)-11-oxo1,5,6,7,8,9,10 10a-octahydro-1,4-(epoxymethano)benzo[8]annulen-4a(4*H*)-yl)acetaldehyde (*Endo*-30). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (66.8 mg combined, 75% combined yield; 45.0 mg, 51% yield ***Endo*-30**; 21.8 mg, 24% yield ***Exo*-30**) as a pale yellow oil. The *dr* was 2.3:1 as determined by crude ^1H NMR. ***Endo*-30**: R_f = 0.14 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –1.90° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2927, 2855, 1757, 1717, 1643, 1263 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.74 (d, *J* = 1.7 Hz, 1 H), 7.29 (dt, *J* = 6.5, 1.7 Hz, 1 H), 5.36 (d, *J* = 2.0 Hz, 1 H), 3.81 (d, *J* = 1.3 Hz, 3 H), 3.76 (d, *J* = 6.4 Hz, 1 H), 2.97 (d, *J* = 17.0 Hz, 1 H), 2.15 (d, *J* = 17.0 Hz, 1 H), 2.09 (dd, *J* = 15.5, 5.1 Hz, 1 H), 2.01–1.90 (m, 1 H), 1.83–1.12 (m, 11 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.69, 171.46, 162.79, 141.40, 135.69, 81.85, 55.04, 52.41, 50.73, 46.76, 42.33, 33.77, 29.41, 28.42, 26.39, 26.36, 25.58; HRMS (ESI) calcd for $C_{17}H_{23}O_5^+$ $[M + H]^+$ 307.1540, found 307.1545. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a

Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 98:2, flow rate of 1.0 mL/min, 254 nm) R_t = 48.05 min (minor), R_t = 52.35 min (major), 59% *ee*.

***Exo*-30**: R_f = 0.25 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –32.56° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2928, 2855, 1759, 1717, 1636, 1258 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.78 (d, *J* = 1.7 Hz, 1 H), 7.30 (dd, *J* = 6.6, 2.3 Hz, 1 H), 5.39 (dd, *J* = 4.0, 2.3 Hz, 1 H), 3.98 (d, *J* = 6.7 Hz, 1 H), 3.81 (s, 3 H), 3.16 (dd, *J* = 18.3, 1.8 Hz, 1 H), 2.48 (d, *J* = 18.3 Hz, 1 H), 2.03 (ddd, *J* = 15.1, 5.9, 2.5 Hz, 1 H), 1.75 (dd, *J* = 9.7, 3.9 Hz, 1 H), 1.73–1.58 (m, 3 H), 1.53–1.37 (m, 4 H), 1.31–1.08 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.11, 171.87, 163.14, 140.25, 135.82, 79.11, 53.92, 52.43, 52.27, 49.28, 43.23, 33.16, 29.12, 26.30, 25.97, 25.76, 25.34; HRMS (ESI) calcd for $C_{17}H_{23}O_5^+$ $[M + H]^+$ 307.1540, found 307.1532. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 18.88 min (minor), R_t = 30.12 min (major), 2% *ee*.



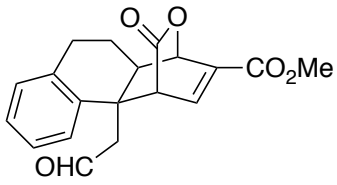
Methyl (1*R*,4*R*,4a*R*,14a*R*)-15-oxo-4a-(2-oxoethyl)-1,4,4a,5,6,7,8,9,10,11,12,13,14,14a-tetradecahydro-1,4-(epoxymethano)benzo[12]annulene-2-carboxylate (*Endo*-31). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (47.1 mg, 47% yield ***Endo*-31**) as a colorless oil. The *dr* was >20:1 as determined by crude ^1H NMR. ***Endo*-31**: R_f = 0.37 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –6.86° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2931, 2861, 1763, 1719, 1639, 1258 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (d, *J* = 2.1 Hz, 1 H), 7.18 (dd, *J* = 6.5, 2.3 Hz, 1 H), 5.42 (d, *J* = 2.3 Hz, 1 H), 3.96 (d, *J* = 6.5 Hz, 1 H), 3.83 (s, 3 H), 2.70 (dd, *J* = 17.2, 2.2 Hz, 1 H), 2.45 (d, *J* = 17.1 Hz, 1 H), 1.84–1.75 (m, 1 H), 1.72 (dd, *J* = 9.6, 3.4 Hz, 1 H), 1.65–1.54 (m, 3 H), 1.43–1.21 (m, 11 H), 1.19–1.06 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.97, 171.95, 162.61, 138.50, 136.98, 77.22, 52.41, 51.28, 46.91, 43.56, 40.32, 37.64, 28.23, 26.54, 25.72, 24.77, 24.09, 24.06, 23.97, 23.92, 22.54; HRMS (ESI) calcd for $C_{21}H_{31}O_5^+$ $[M + H]^+$ 363.2166, found 363.2174. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 8.46 min (minor), R_t = 10.25 min (major), 21% *ee*.



Methyl (1*R*,4*R*,4a*S*,9a*R*)-10-oxo-4a-(2-oxoethyl)-4,4a,9,9a-tetrahydro-1*H*-1,4-(epoxymethano)fluorene-2-carboxylate (*Endo*-32). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (65.5 mg combined, 70% combined yield; 42.6 mg, 46% yield ***Endo*-32**; 22.9 mg, 24% yield ***Exo*-32**) as a pale yellow oil. The *dr* was 2.2:1 as determined by crude ^1H NMR. ***Endo*-32**: R_f = 0.12 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –119.50° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2953, 2851, 1762, 1720, 1634, 1254, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1 H), 7.36 (dd, *J* = 6.3, 2.1 Hz, 1 H), 7.25 (t, *J* = 4.4 Hz, 3 H), 7.20 (q, *J* = 4.2 Hz, 1 H), 5.62 (d, *J* = 2.1 Hz, 1 H), 3.91 (d, *J* = 6.3 Hz, 1 H), 3.84 (s, 3 H), 3.49 (dd, *J* = 17.1, 10.1 Hz, 1 H), 3.15 (dd, *J* = 17.1, 3.1 Hz, 1 H), 3.00 (dd, *J* = 16.0, 1.5 Hz, 1 H), 2.65 (dt, *J* = 10.1, 2.5 Hz, 1 H), 2.60 (dd, *J* = 16.1, 2.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.49, 169.80, 162.51, 143.14, 141.75, 139.48, 137.16, 129.35, 127.84, 125.69, 123.26, 78.24, 53.68, 53.31, 53.19, 52.55, 46.56, 34.58; HRMS (ESI) calcd for $C_{18}H_{15}NO_4^+$ [M +

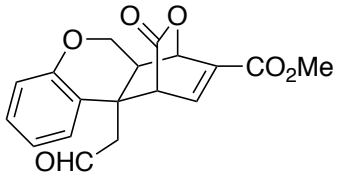
H – H_2O]$^+$ 295.0965, found 295.0972. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 21.19 min (major), R_t = 25.69 min (minor), 98% *ee*.

***Exo*-32**: R_f = 0.27 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –77.24° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2953, 2852, 1759, 1719, 1636, 1259, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (d, *J* = 1.6 Hz, 1 H), 7.18 (dd, *J* = 5.8, 3.1 Hz, 2 H), 7.16–7.10 (m, 1 H), 7.10–7.05 (m, 1 H), 6.83 (dd, *J* = 6.5, 2.3 Hz, 1 H), 5.70 (dd, *J* = 4.4, 2.3 Hz, 1 H), 3.92 (d, *J* = 6.5 Hz, 1 H), 3.71 (s, 3 H), 3.37 (dd, *J* = 17.3, 10.2 Hz, 1 H), 3.22 (dd, *J* = 17.1, 1.4 Hz, 1 H), 3.14 (ddd, *J* = 10.2, 4.4, 3.2 Hz, 1 H), 2.88 (dd, *J* = 17.1, 1.8 Hz, 1 H), 2.55 (dd, *J* = 17.4, 3.2 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.72, 171.03, 163.36, 143.09, 142.35, 140.89, 134.12, 128.87, 127.73, 125.27, 122.18, 76.77, 53.21, 52.74, 52.52, 52.41, 46.97, 33.42; HRMS (ESI) calcd for $C_{18}H_{15}NO_4^+$ [M + H – H_2O]$^+$ 295.0965, found 295.0974. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 97:3, flow rate of 1.0 mL/min, 215 nm) R_t = 38.51 min (minor), R_t = 46.08 min (major), 73% *ee*.



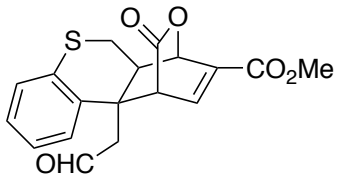
Methyl (1*R*,4*R*,4a*S*,10a*R*)-11-oxo-4a-(2-oxoethyl)-1,4,4a,9,10,10a-hexahydro-1,4-(epoxymethano)phenanthrene-2-carboxylate (*Endo*-33). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (66.0 mg combined, 68% combined yield; 45.5 mg, 47% yield ***Endo*-33**; 20.5 mg, 21% yield ***Exo*-33**) as a colorless oil. The *dr* was 2.3:1 as determined by crude ^{1}H NMR. ***Endo*-33**: R_f = 0.10 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –86.98° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2950, 2852, 1763, 1719, 1638, 1254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1 H), 7.49 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.38 (dd, *J* = 6.5, 2.3 Hz, 1 H), 7.28 (td, *J* = 7.6, 1.8 Hz, 1 H), 7.22–7.13 (m, 2 H), 5.50 (dd, *J* = 2.3, 1.1 Hz, 1 H), 4.23 (d, *J* = 6.4 Hz, 1 H), 3.84 (s, 3 H), 2.87 (ddd, *J* = 15.7, 6.9, 3.9 Hz, 1 H), 2.70 (dd, *J* = 14.2, 2.4 Hz, 1 H), 2.68–2.61 (m, 1 H), 2.44 (dd, *J* = 14.2, 3.1 Hz, 1 H), 2.24–2.10 (m, 2 H), 1.91–1.82 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.46, 169.86, 162.44, 139.06, 138.97, 137.95, 136.11, 129.48, 127.79, 127.58, 126.53, 78.47, 55.84, 52.52, 52.14, 44.39, 40.78, 28.37, 26.56; HRMS (ESI) calcd for $C_{19}H_{17}O_4^+$ [M + H – H_2O]$^+$ 309.1121, found 309.1130. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 20.27 min (major), R_t = 23.07 min (minor), 99% *ee*.

***Exo*-33**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –44.28° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2950, 2854, 1761, 1719, 1637, 1254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (dd, *J* = 3.3, 1.7 Hz, 1 H), 7.38 (dd, *J* = 7.9, 1.4 Hz, 1 H), 7.29–7.23 (m, 1 H), 7.17 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.06 (td, *J* = 7.0, 1.8 Hz, 2 H), 5.58 (dd, *J* = 3.2, 2.3 Hz, 1 H), 4.35 (d, *J* = 6.4 Hz, 1 H), 3.73 (s, 3 H), 3.00 (dd, *J* = 15.0, 1.7 Hz, 1 H), 2.74 (ddd, *J* = 9.6, 6.8, 3.2 Hz, 1 H), 2.64 (dd, *J* = 15.0, 3.3 Hz, 1 H), 2.58 (td, *J* = 10.5, 10.0, 5.0 Hz, 1 H), 2.48 (ddd, *J* = 15.8, 6.8, 4.3 Hz, 1 H), 2.22 (dtd, *J* = 13.6, 6.8, 4.4 Hz, 1 H), 1.18 (dtd, *J* = 13.7, 9.7, 4.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.38, 171.26, 163.05, 140.44, 138.25, 136.69, 136.02, 129.32, 127.66, 127.51, 125.60, 77.48, 56.97, 52.44, 52.42, 45.92, 41.51, 27.97, 25.43; HRMS (ESI) calcd for $C_{19}H_{19}O_5^+$ [M + H]$^+$ 327.1227, found 327.1235. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 215 nm) R_t = 15.96 min (minor), R_t = 18.04 min (major), 96% *ee*.



Methyl (6a*S*,7*R*,10*R*,10a*S*)-11-oxo-10a-(2-oxoethyl)-6a,7,10,10a-tetrahydro-6*H*-7,10-(epoxymethano)benzo[*c*]chromene-8-carboxylate (*Endo*-34). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (60.1 mg combined, 68% combined yield; 52.6 mg, 60% yield ***Endo*-34**; 7.5 mg, 8% yield ***Exo*-34**) as an amorphous pale yellow solid. The *dr* was 4.9:1 as determined by crude ^{1}H NMR. ***Endo*-34**: R_f = 0.07 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –80.60° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2954, 2853, 1767, 1720, 1490, 1253, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (dd, *J* = 2.8, 1.8 Hz, 1 H), 7.41 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.37 (dd, *J* = 6.4, 2.1 Hz, 1 H), 7.21 (ddd, *J* = 8.4, 7.4, 1.6 Hz, 1 H), 7.06 (td, *J* = 7.5, 1.3 Hz, 1 H), 6.95 (dd, *J* = 8.1, 1.3 Hz, 1 H), 5.62 (dd, *J* = 2.3, 1.2 Hz, 1 H), 4.45 (dd, *J* = 11.7, 5.6 Hz, 1 H), 4.19 (dd, *J* = 11.7, 6.0 Hz, 1 H), 4.03 (d, *J* = 6.4 Hz, 1 H), 3.85 (s, 3 H), 2.97 (dd, *J* = 15.1, 1.8 Hz, 1 H), 2.48 (dd, *J* = 15.1, 2.8 Hz, 1 H), 2.35 (td, *J* = 5.8, 1.2 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.71, 169.03, 162.20, 156.00, 138.95, 137.65, 129.61, 126.53, 124.97, 123.33, 118.70, 76.45, 67.69, 54.77, 53.44, 52.69, 44.53, 37.94; HRMS (ESI) calcd for $C_{18}H_{15}O_5^+$ $[M + H - H_2O]^+$ 311.0914, found 311.0920. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralcel AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 30.56 min (major), R_t = 38.12 min (minor), 98% *ee*.

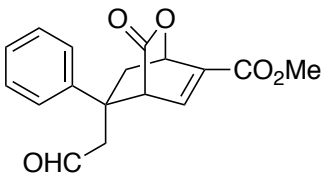
***Exo*-34**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –74.88° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2954, 2852, 1757, 1720, 1489, 1290 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (t, *J* = 1.5 Hz, 1 H), 7.27 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.13 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1 H), 6.98 (td, *J* = 7.5, 1.3 Hz, 1 H), 6.78 (dd, *J* = 8.1, 1.3 Hz, 1 H), 6.67 (dd, *J* = 6.4, 2.2 Hz, 1 H), 5.71 (dd, *J* = 3.2, 2.1 Hz, 1 H), 4.28 (dd, *J* = 12.0, 4.1 Hz, 1 H), 4.23 (dd, *J* = 12.0, 1.5 Hz, 1 H), 3.77 (s, 3 H), 3.68–3.61 (m, 2 H), 2.79–2.71 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.61, 170.81, 162.65, 155.37, 138.38, 135.94, 129.00, 125.17, 125.08, 122.93, 118.55, 77.36, 64.61, 54.88, 54.05, 52.42, 47.18, 38.60; HRMS (ESI) calcd for $C_{18}H_{15}O_5^+$ $[M + H - H_2O]^+$ 311.0914, found 311.0923. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak OD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 205 nm) R_t = 34.71 min (major), R_t = 49.92 min (minor), 94% *ee*.



Methyl (6a*R*,7*R*,10*R*,10a*R*)-11-oxo-10a-(2-oxoethyl)-6a,7,10,10a-tetrahydro-6*H*-7,10-(epoxymethano)benzo[*c*]thiochromene-8-carboxylate (*Endo*-35). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 1:1) to afford the desired product (48.2 mg combined, 47% combined yield; 27.0 mg, 26% yield ***Endo*-35**; 21.2 mg, 21% yield ***Exo*-35**) as a pale yellow oil. The *dr* was 1.2:1 as determined by crude ^{1}H NMR. ***Endo*-35**: R_f = 0.17 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = +16.10° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2952, 1762, 1717, 1268, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (dd, *J* = 3.0, 2.1 Hz, 1 H), 7.63 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.42 (ddd, *J* = 6.6, 3.2, 1.9 Hz, 2 H), 7.22 (dtd, *J* = 25.2, 7.4, 1.6 Hz, 2 H), 5.47 (dd, *J* = 2.4, 1.1 Hz, 1 H), 4.70 (d, *J* = 6.7 Hz, 1 H), 3.86 (s, 3 H), 3.11 (dd, *J* = 13.0, 5.7 Hz, 1 H), 2.95 (dd, *J* = 14.5, 2.2 Hz, 1 H), 2.75 (t, *J* = 13.0 Hz, 1 H), 2.46 (ddd, *J* = 12.9, 5.7, 1.1 Hz, 1 H), 2.26 (dd, *J* = 14.4, 3.1 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.06, 169.43, 162.25, 138.94, 137.88, 137.39, 136.52, 130.93, 128.22, 127.87, 127.15, 76.53, 54.74, 52.67, 51.24, 48.20, 42.56, 31.82; HRMS (ESI) calcd for $C_{18}H_{15}O_4S^+$ [M +

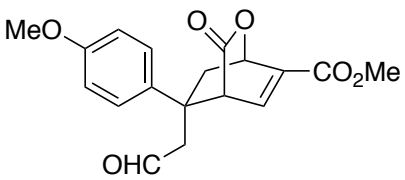
H]$^+$ 327.0695, found 327.0694. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 44.35 min (minor), R_t = 51.25 min (major), 93% *ee*.

***Exo*-35**: R_f = 0.23 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –10.60° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2952, 2851, 1762, 1718, 1260, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (t, *J* = 1.9 Hz, 1 H), 7.42 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.27–7.24 (m, 1 H), 7.21 (td, *J* = 7.7, 1.7 Hz, 1 H), 7.15 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.07 (dd, *J* = 6.4, 2.2 Hz, 1 H), 5.57 (t, *J* = 2.5 Hz, 1 H), 4.42 (d, *J* = 6.3 Hz, 1 H), 3.75 (s, 3 H), 3.28 (dd, *J* = 13.4, 5.2 Hz, 1 H), 3.06–2.99 (m, 2 H), 2.96 (dd, *J* = 16.3, 2.3 Hz, 1 H), 2.30 (dd, *J* = 13.3, 9.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.46, 170.81, 162.86, 139.02, 136.51, 135.55, 130.30, 127.54, 127.19, 127.08, 76.60, 55.81, 52.48, 51.57, 51.12, 42.71, 29.76; HRMS (ESI) calcd for $C_{18}H_{15}O_4S^+$ $[M+H]^+$ 327.0695, found 327.0696. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 37.16 min (minor), R_t = 46.02 min (major), 93% *ee*.



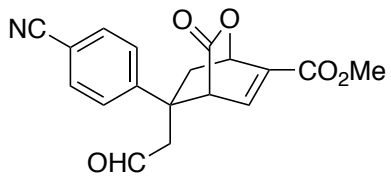
Methyl (1*R*,4*R*,8*R*)-3-oxo-8-(2-oxoethyl)-8-phenyl-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (*Endo*-36). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (56.8 mg combined, 63% combined yield; 29.5 mg, 33% yield ***Endo*-36**; 27.3 mg, 30% yield ***Exo*-36**) as a colorless oil. The *dr* was 1.1:1 as determined by crude ^{1}H NMR. ***Endo*-36**: R_f = 0.13 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –45.90° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2954, 2852, 1761, 1718, 1637, 1438, 1264 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (t, *J* = 2.0 Hz, 1 H), 7.48–7.41 (m, 3 H), 7.37 (t, *J* = 7.9 Hz, 2 H), 7.30–7.23 (m, 1 H), 5.75 (dt, *J* = 4.0, 1.9 Hz, 1 H), 4.26 (d, *J* = 6.6 Hz, 1 H), 3.85 (s, 3 H), 3.05 (dd, *J* = 14.2, 4.1 Hz, 1 H), 2.79 (dd, *J* = 15.8, 2.6 Hz, 1 H), 2.72 (dd, *J* = 15.8, 1.7 Hz, 1 H), 2.07 (dd, *J* = 14.2, 1.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.81, 170.26, 162.45, 142.34, 140.17, 137.24, 129.24, 127.86, 126.83, 73.64, 55.13, 52.57, 50.82, 43.07, 39.82; HRMS (ESI) calcd for $C_{17}H_{15}O_5^+$ $[M + H – H_2O]^+$ 283.0965, found 283.0966. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 20.97 min (minor), R_t = 29.31 min (major), 90% *ee*.

***Exo*-36**: R_f = 0.25 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –25.00° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2953, 2851, 1763, 1718, 1636, 1261, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1 H), 7.33 (d, *J* = 1.1 Hz, 2 H), 7.28–7.20 (m, 3 H), 7.14 (dd, *J* = 6.3, 2.2 Hz, 1H), 5.77–5.74 (m, 1 H), 4.33 (d, *J* = 6.3 Hz, 1 H), 3.74 (s, 3 H), 3.11 (dd, *J* = 16.9, 1.6 Hz, 1 H), 2.91 (dd, *J* = 16.9, 1.7 Hz, 1 H), 2.59–2.54 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.59, 171.42, 162.46, 142.36, 140.17, 136.20, 129.18, 127.55, 126.64, 73.71, 56.43, 52.39, 51.51, 42.69, 39.11; HRMS (ESI) calcd for $C_{17}H_{15}O_5^+$ $[M + H – H_2O]^+$ 283.0965, found 283.0973. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 30.48 min (minor), R_t = 34.23 min (major), 72% *ee*.



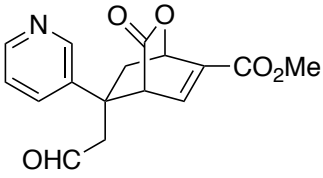
Methyl (1*R*,4*R*,8*R*)-8-(4-methoxyphenyl)-3-oxo-8-(2-oxo ethyl)-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (*Endo*-37). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (64.2 mg combined, 65% combined yield; 33.4 mg, 34% yield ***Endo*-37**; 30.8 mg, 31% yield ***Exo*-37**) as a colorless oil. The *dr* was 1.3:1 as determined by crude ^{1}H NMR. ***Endo*-37**: R_f = 0.16 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –73.70° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2954, 2839, 760, 1720, 1516, 1253 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (dd, *J* = 2.5, 1.7 Hz, 1 H), 7.41 (dd, *J* = 6.5, 2.4 Hz, 1 H), 7.35 (d, *J* = 8.9 Hz, 2 H), 6.89 (d, *J* = 8.9 Hz, 2 H), 5.74 (dt, *J* = 4.1, 1.8 Hz, 1 H), 4.19 (d, *J* = 6.6 Hz, 1 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 3.02 (dd, *J* = 14.2, 4.1 Hz, 1 H), 2.76 (dd, *J* = 15.7, 2.6 Hz, 1 H), 2.67 (dd, *J* = 15.7, 1.8 Hz, 1 H), 2.04 (dd, *J* = 14.3, 1.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.08, 170.36, 162.47, 158.92, 140.13, 137.14, 134.12, 128.01, 114.53, 73.65, 55.39, 55.15, 52.55, 51.31, 42.50, 39.66; HRMS (ESI) calcd for $C_{18}H_{19}O_6^+$ $[M + H]^+$ 331.1176, found 331.1173. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 240 nm) R_t = 30.15 min (minor), R_t = 33.32 min (major), 88% *ee*.

***Exo*-37**: R_f = 0.26 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –51.70° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2954, 2839, 1760, 1719, 1636, 1515, 1259 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (t, *J* = 1.7 Hz, 1 H), 7.12 (m, 3 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 5.74 (q, *J* = 2.6 Hz, 1 H), 4.26 (d, *J* = 6.3 Hz, 1 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.08 (dd, *J* = 16.8, 1.7 Hz, 1 H), 2.85 (dd, *J* = 16.8, 1.8 Hz, 1 H), 2.56–2.52 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.90, 171.46, 162.51, 158.70, 140.29, 135.98, 134.09, 127.72, 114.44, 73.75, 56.44, 55.38, 52.37, 51.93, 42.10, 38.93; HRMS (ESI) calcd for $C_{18}H_{19}O_6^+$ $[M + H]^+$ 331.1176, found 331.1172. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 215 nm) R_t = 20.42 min (major), R_t = 23.67 min (major), 55% *ee*.



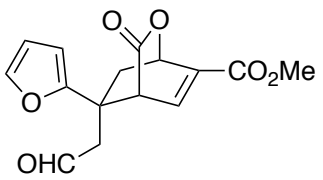
Methyl (1*R*,4*R*,8*R*)-8-(4-cyanophenyl)-3-oxo-8-(2-oxoethyl)-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (*Endo*-38). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 1:1) to afford the desired product (62.4 mg combined, 65% combined yield; 41.2 mg, 43% yield ***Endo*-38**; 21.2 mg, 22% yield ***Exo*-38**) as a yellow oil. The *dr* was 1.8:1 as determined by crude ^{1}H NMR. ***Endo*-38**: R_f = 0.07 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –73.72° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2955, 2851, 2292, 1761, 1719, 1639, 1269, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (t, *J* = 1.3 Hz, 1 H), 7.67 (d, *J* = 8.6 Hz, 2 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 7.42 (dd, *J* = 6.6, 2.3 Hz, 1 H), 5.81–5.74 (m, 1 H), 4.33 (d, *J* = 6.6 Hz, 1 H), 3.87 (s, 3 H), 3.00 (dd, *J* = 14.4, 4.1 Hz, 1 H), 2.97–2.91 (m, 1 H), 2.85 (d, *J* = 17.2 Hz, 1 H), 2.09 (dd, *J* = 14.4, 1.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.12, 169.78, 162.19, 147.97, 139.47, 137.60, 132.74, 127.89, 118.20, 111.81, 73.44, 54.88, 52.65, 50.27, 43.09, 39.99; HRMS (ESI) calcd for $C_{18}H_{14}NO_4^+$ $[M + H – H_2O]^+$ 308.0917, found 308.0917. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 240 nm) R_t = 78.37 min (major), R_t = 87.08 min (major), 90% *ee*.

***Exo*-38**: R_f = 0.17 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –51.92° (*c* = 1.0 in $CHCl_3$). IR (thin film) 2954, 2920, 2851, 2228, 1761, 1719, 1638, 1261 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1 H), 7.62 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 7.11 (dd, *J* = 6.3, 2.2 Hz, 1 H), 5.75 (dt, *J* = 3.6, 2.1 Hz, 1 H), 4.35 (d, *J* = 6.2 Hz, 1 H), 3.75 (s, 3 H), 3.20 (d, *J* = 18.2 Hz, 1 H), 3.05 (d, *J* = 18.2 Hz, 1 H), 2.55 (dd, *J* = 6.3, 2.8 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.34, 170.73, 162.18, 148.08, 139.37, 136.86, 132.73, 127.74, 118.13, 111.63, 73.43, 56.28, 52.53, 50.74, 42.84, 39.51; HRMS (ESI) calcd for $C_{18}H_{14}NO_4^+$ $[M + H - H_2O]^+$ 308.0917, found 308.0920. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak OD-H column (hexanes/*i*PrOH, 85:15, flow rate of 1.0 mL/min, 240 nm) R_t = 40.82 min (minor), R_t = 43.96 min (major), 79% *ee*.



Methyl (1*R*,4*R*,8*R*)-3-oxo-8-(2-oxoethyl)-8-(pyridin-3-yl)-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (*Endo*-39). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 2:1) to afford the desired product (75.0 mg combined, 83% combined yield; 64.3 mg, 71% yield ***Endo*-39**; 10.7 mg, 12% yield ***Exo*-39**) as a pale yellow oil. The *dr* was 5.7:1 as determined by crude ^1H NMR. ***Endo*-39**: R_f = 0.17 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –12.18° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2955, 2853, 1759, 1721, 1279, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.42 (s, 1 H), 8.70 (d, *J* = 2.6 Hz, 1 H), 8.50 (dd, *J* = 4.8, 1.5 Hz, 1 H), 7.85 (ddd, *J* = 8.2, 2.7, 1.5 Hz, 1 H), 7.41 (dd, *J* = 6.6, 2.4 Hz, 1 H), 7.30 (dd, *J* = 8.1, 4.8 Hz, 1 H), 5.76 (dt, *J* = 4.1, 1.9 Hz, 1 H), 4.36 (d, *J* = 6.5 Hz, 1 H), 3.85 (s, 3 H), 3.02 (dd, *J* = 14.4, 4.0 Hz, 1 H), 2.92 (dd, *J* = 17.2, 1.6 Hz, 1 H), 2.84 (dd, *J* = 17.2, 1.2 Hz, 1 H), 2.08 (dd, *J* = 14.3, 1.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.37, 169.84, 162.26, 148.80, 148.70, 139.54, 138.51, 137.52, 134.58, 123.52, 73.47, 55.02, 52.64, 50.15, 41.52, 39.86; HRMS (ESI) calcd for $C_{16}H_{16}NO_5^+$ $[M + H]^+$ 302.1023, found 302.1024. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak OD-H column (hexanes/*i*PrOH, 80:20, flow rate of 1.0 mL/min, 215 nm) R_t = 34.54 min (major), R_t = 40.94 min (minor), 94% *ee*.

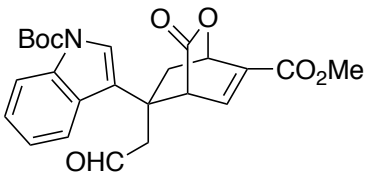
***Exo*-39**: R_f = 0.27 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –23.16° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2954, 2853, 1760, 1719, 1638, 1262 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1 H), 8.54 (d, *J* = 2.7 Hz, 1 H), 8.47 (dd, *J* = 4.8, 1.5 Hz, 1 H), 7.57 (ddd, *J* = 8.2, 2.7, 1.5 Hz, 1 H), 7.29–7.24 (m, 1 H), 7.12 (dd, *J* = 6.3, 2.2 Hz, 1 H), 5.78–5.74 (m, 1 H), 4.36 (d, *J* = 6.3 Hz, 1 H), 3.75 (s, 3 H), 3.26–3.20 (m, 1 H), 3.04 (dd, *J* = 18.2, 1.0 Hz, 1 H), 2.57 (t, *J* = 2.4 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.52, 170.83, 162.24, 148.63, 148.30, 139.52, 138.31, 136.77, 134.63, 123.56, 73.50, 56.26, 52.51, 50.84, 41.23, 38.97; HRMS (ESI) calcd for $C_{16}H_{14}NO_4^+$ $[M + H - H_2O]^+$ 284.0917, found 284.0913. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak OD-H column (hexanes/*i*PrOH, 80:20, flow rate of 1.0 mL/min, 254 nm) R_t = 20.89 min (minor), R_t = 26.04 min (major), 55% *ee*.



Methyl (1*R*,4*R*,8*R*)-8-(furan-2-yl)-3-oxo-8-(2-oxoethyl)-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (Endo-40). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (40.4 mg combined, 46% combined yield; 25.9 mg, 29% yield ***Endo*-40**; 14.5 mg, 17% yield ***Exo*-40**) as a yellow oil. The

dr was 1.8:1 as determined by crude ^{1}H NMR. ***Endo*-40**: R_f = 0.10 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –95.32° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2955, 1764, 1720, 1635, 1274, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1 H), 7.31 (dd, *J* = 1.8, 0.9 Hz, 1 H), 7.03 (dd, *J* = 6.5, 2.2 Hz, 1 H), 6.25 (dd, *J* = 3.3, 1.9 Hz, 1 H), 5.99 (dd, *J* = 3.4, 0.9 Hz, 1 H), 5.76 (dd, *J* = 3.7, 1.9 Hz, 1 H), 4.01 (d, *J* = 6.4 Hz, 1 H), 3.79 (s, 3 H), 3.24 (dd, *J* = 16.8, 1.6 Hz, 1 H), 2.73 (dd, *J* = 16.7, 1.9 Hz, 1 H), 2.46 (dd, *J* = 14.5, 3.7 Hz, 1 H), 2.38 (dd, *J* = 14.5, 1.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.37, 170.51, 162.55, 154.52, 142.52, 139.80, 136.23, 110.69, 107.71, 73.88, 52.96, 52.46, 51.74, 39.03, 37.50; HRMS (ESI) calcd for $C_{15}H_{15}O_6^+$ $[M + H]^+$ 291.0863, found: 291.0868. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 38.01 min (minor), R_t = 81.61 min (major), 91% *ee*.

***Exo*-40**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –17.82° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2955, 2852, 1761, 1721, 1638, 1261, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (t, *J* = 2.1 Hz, 1 H), 7.38 (dd, *J* = 1.8, 0.9 Hz, 1 H), 7.35 (dd, *J* = 6.5, 2.3 Hz, 1 H), 6.32–6.30 (m, 2 H), 5.77–5.71 (m, 1 H), 4.00 (d, *J* = 6.5 Hz, 1 H), 3.84 (s, 3 H), 2.93–2.88 (m, 2 H), 2.59 (dd, *J* = 15.7, 2.2 Hz, 1 H), 1.93 (dd, *J* = 14.3, 1.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.16, 169.82, 162.34, 154.60, 143.15, 139.02, 137.45, 110.80, 107.93, 73.16, 52.60, 51.85, 51.65, 39.56, 37.13; HRMS (ESI) calcd for $C_{15}H_{15}O_6^+$ $[M + H]^+$ 291.0863, found 291.0872. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralcel OD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 240 nm) R_t = 40.97 min (minor), R_t = 44.37 min (major), 18% *ee*.

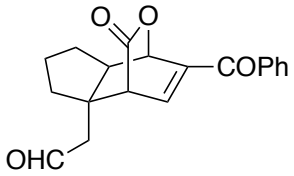


***tert-B*utyl 3-((1*R*,4*R*,5*R*)-7-(methoxycarbonyl)-3-oxo-5-(2-oxoethyl)-2-oxabicyclo[2.2.2]oct-7-en-5-yl)-1*H*-indole-1-carboxylate (*Endo*-41).** Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 2:1) to afford the desired product (77.0 mg combined, 89% combined yield; 39.3 mg, 45% yield ***Endo*-41**; 37.7 mg, 44% yield ***Exo*-41**) as a yellow oil. The *dr* was 1.4:1 as determined by crude ^{1}H NMR. ***Endo*-41**: R_f = 0.10 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –28.68° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2979, 1762, 1723, 1636, 1374, 1157, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1 H), 8.23 (d, *J* = 8.4 Hz, 1 H), 7.71 (s, 1 H), 7.52 (d, *J* = 7.9 Hz, 1 H), 7.46 (dd, *J* = 6.6, 2.3 Hz, 1 H), 7.36 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1 H), 7.30–7.24 (m, 1 H), 5.75 (dt, *J* = 3.9, 1.9 Hz, 1 H), 4.42 (d, *J* = 6.6 Hz, 1 H), 3.86 (s, 3 H), 3.08 (dd, *J* = 15.2, 1.8 Hz, 1 H), 2.95 (dd, *J* = 13.9, 3.9 Hz, 1 H), 2.63 (dd, *J* = 15.1, 3.1 Hz, 1 H), 2.12 (dd, *J* = 13.9, 1.8 Hz, 1 H), 1.67 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.14, 170.55, 162.44, 149.32, 139.78, 137.10, 136.50, 127.92, 125.04, 123.60, 122.93, 121.49, 119.98, 116.24, 84.47, 73.52, 52.56, 51.23, 49.69, 39.47, 38.59, 28.26; HRMS (ESI) calcd for $C_{24}H_{24}NO_6^+$ $[M + H - H_2O]^+$ 422.1598, found 422.1605. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak OD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 19.43 min (major), R_t = 23.22 min (minor), 93% *ee*.

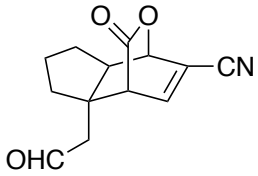
***Exo*-41**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –5.84° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2979, 2852, 1763, 1724, 1374, 1156, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (t, *J* = 1.9 Hz, 1 H), 8.20–8.07 (m, 1 H), 7.60 (d, *J* = 7.9 Hz, 1 H), 7.38–7.31 (m, 2 H), 7.30–7.24 (m, 1 H), 7.18 (dd, *J* = 6.5, 2.2 Hz, 1 H), 5.77 (dt, *J* = 3.9, 1.9 Hz, 1 H), 4.54 (d, *J* = 6.5 Hz, 1 H), 3.75

(s, 3 H), 3.19 (d, J = 16.4 Hz, 1 H), 3.05 (dd, J = 16.5, 2.2 Hz, 1 H), 2.61 (dd, J = 14.1, 3.9 Hz, 1 H), 2.45 (dd, J = 14.0, 1.8 Hz, 1 H), 1.68 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.68, 170.86, 162.49, 149.46, 140.08, 136.39, 135.74, 127.42, 125.25, 123.59, 123.09, 121.52, 119.85, 116.24, 84.86, 73.62, 52.85, 52.40, 50.60, 38.72, 38.50, 28.35; HRMS (ESI) calcd for $C_{24}H_{24}NO_6^+$ [M + H – H_2O]$^+$ 422.1598, found 422.1604. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 205 nm) R_t = 9.07 min (minor), R_t = 11.91 min (major), 16% *ee*.

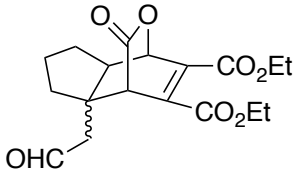
NOTE: As a result of the larger diastereoselectivity when altering the pyrone partner, the more minor exo diastereomer was not characterized for those compounds shown in Table 3.



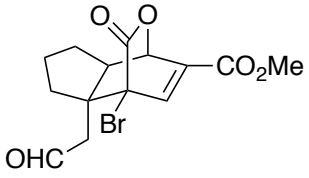
2-((3a*R*,4*R*,7*R*,7a*R*)-5-benzoyl-8-oxo-1,2,3,3a,4,7-hexahydro-7a*H*-4,7-(epoxymethano)inden-7a-yl)acetaldehyde (*Endo*-42). Prepared following the general procedure described above, the crude material was further purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (89.0 mg combined, 96% combined yield; 72.8 mg, 78% yield ***Endo*-42**; 16.2 mg, 18% yield ***Exo*-42**) as an off-white amorphous solid. The *dr* was 5.1:1 as determined by crude ^{1}H NMR. ***Endo*-42**: R_f = 0.21 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = –9.70° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2957, 2873, 1758, 1721, 1644, 1258 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1 H), 7.74 (d, J = 7.7 Hz, 2 H), 7.61 (t, J = 7.4 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 3 H), 6.98 (dd, J = 6.3, 2.1 Hz, 1 H), 5.61 (d, J = 1.8 Hz, 1 H), 3.84 (d, J = 6.3 Hz, 1 H), 2.55 (d, J = 16.5 Hz, 1 H), 2.36 (dd, J = 16.5, 2.3 Hz, 1 H), 2.09 (m, 2 H), 1.96–1.81 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.98, 190.84, 171.80, 141.25, 133.45, 130.32, 129.41, 128.89, 128.63, 78.38, 53.31, 51.47, 50.03, 49.00, 36.24, 28.66, 27.35; HRMS (ESI) calcd for $C_{19}H_{17}O_3^+$ [M + H]$^+$ 293.1183, found 293.1183. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 97:3, flow rate of 1.0 mL/min, 254 nm) R_t = 38.55 min (minor), R_t = 52.30 min (major), 89% *ee*.



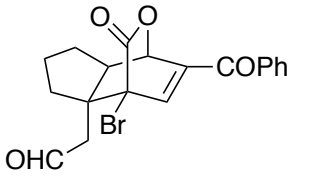
(3a*R*,4*R*,7*R*,7a*R*)-8-oxo-7a-(2-oxoethyl)-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-(epoxymethano)indene-5-carbonitrile (*Endo*-43). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (50.6 mg combined, 73% combined yield; 47.1 mg, 68% yield ***Endo*-43**; 3.5 mg, 5% yield ***Exo*-43**) as a white amorphous solid. The *dr* was 9.8:1 as determined by crude ^{1}H NMR. ***Endo*-43**: R_f = 0.14 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{24}$ = –7.53° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2960, 2873, 2224, 1762, 1720, 1655, 1588 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (d, J = 1.6 Hz, 1 H), 7.24 (dd, J = 6.4, 2.1 Hz, 1 H), 5.13 (t, J = 1.7 Hz, 1 H), 3.90 (d, J = 6.4 Hz, 1 H), 2.61 (d, 17.3 Hz, 1 H), 2.44 (dd, J = 17.2, 1.8 Hz, 1 H), 2.13–2.05 (m, 1 H), 1.91–1.72 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.30, 146.95, 118.98, 113.96, 78.54, 52.84, 51.29, 49.55, 48.03, 36.06, 28.45, 27.19; HRMS (ESI) calcd for $C_{13}H_{11}NO_4^+$ [M + H]$^+$ 214.0862, found 214.0860. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 88:12, flow rate of 1.0 mL/min, 254 nm) R_t = 14.19 min (major), R_t = 17.85 min (minor), 89% *ee*.



Diethyl (3a*R*,4*R*,7*S*,7a*R*)-8-oxo-7a-(2-oxoethyl)-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-(epoxymethano)indene-5,6-dicarboxylate (44). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (96.6 mg combined, 92% combined yield) as a colorless oil which was characterized as a 1.4:1 mixture of diastereomers. The *dr* was 1.4:1 as determined by crude ^{1}H NMR. **44**: R_f = 0.23 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = +0.24° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2962, 2873, 2738, 1766, 1721, 1649, 1277 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (d, *J* = 1.4 Hz, 1 H), 9.70 (d, *J* = 1.2 Hz, 1 H), 5.42 (d, *J* = 4.3 Hz, 1 H), 5.39 (d, *J* = 1.3 Hz, 1 H), 4.36–4.22 (m, 8 H), 4.06 (s, 1 H), 4.02 (s, 1 H), 2.76–2.69 (m, 2 H), 2.69–2.63 (m, 2 H), 2.61–2.51 (m, 2 H), 2.01 (td, *J* = 9.5, 8.5, 4.1 Hz, 2 H), 1.89–1.53 (m, 10 H), 1.38–1.23 (m, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.38, 199.20, 170.59, 170.30, 164.60, 164.18, 162.91, 162.12, 140.95, 139.68, 136.14, 136.05, 78.03, 77.51, 62.43, 62.40, 62.17, 62.09, 53.21, 52.74, 52.19, 51.46, 51.45, 49.82, 47.58, 47.19, 36.13, 35.75, 28.42, 27.23, 26.84, 14.09, 14.07, 14.02; HRMS (ESI) calcd for $C_{18}H_{20}O_6^+$ $[M + H - H_2O]^+$ 333.1333, found 333.1323. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralcel OD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 12.66 min (minor), R_t = 13.43 min (major), 96% *ee*. R_t = 9.85 min (minor), R_t = 16.33 min (major), 87% *ee*.

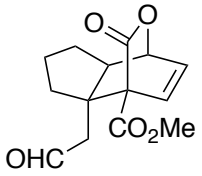


Methyl (3a*R*,4*R*,7*S*,7a*R*)-7-bromo-8-oxo-7a-(2-oxoethyl)-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-(epoxymethano)indene-5-carboxylate (*Endo*-45). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (86.8 mg combined, 89% combined yield; 74.5 mg, 76% yield ***Endo*-45**; 12.3 mg, 13% yield ***Exo*-45**) as a colorless oil. The *dr* was 5.9:1 as determined by crude ^{1}H NMR. ***Endo*-45**: R_f = 0.30 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{24}$ = –3.24° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2955, 2877, 1772, 1722, 1630, 1280, 1255 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (t, *J* = 2.2 Hz, 1 H), 7.26 (d, *J* = 2.1 Hz, 1 H), 5.47 (t, *J* = 2.0 Hz, 1 H), 3.82 (s, 3 H), 3.05 (dd, *J* = 15.9, 2.4 Hz, 1 H), 2.54–2.43 (m, 2 H), 2.27 (ddt, *J* = 12.8, 9.0, 7.5 Hz, 1 H), 2.00–1.69 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.75, 166.85, 161.58, 145.19, 136.64, 77.09, 69.93, 55.50, 52.85, 49.28, 35.43, 30.24, 26.64; HRMS (ESI) calcd for $C_{14}H_{14}BrO_4^+$ $[M + H - H_2O]^+$ 325.0070, found 325.0063. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 13.60 min (major), R_t = 15.23 min (minor), 86% *ee*.

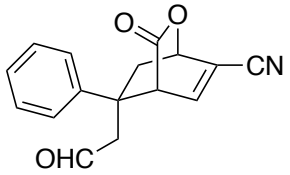


2-((3a*R*,4*R*,7*S*,7a*R*)-5-benzoyl-7-bromo-8-oxo-1,2,3,3a,4,7-hexahydro-7a*H*-4,7-(epoxymethano)inden-7a-yl) acetaldehyde (*Endo*-46). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (76.0 mg combined, 65% combined yield; 57.1 mg, 49% yield ***Endo*-46**; 18.9 mg, 16% yield ***Exo*-46**) as an off-white amorphous solid. The *dr* was 2.9:1 as determined by crude ^{1}H NMR. ***Endo*-46**: R_f = 0.38 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{24}$ = –9.70° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2926, 2871, 1768, 1721, 1649, 1254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (t, *J* = 2.2 Hz, 1 H), 7.78–7.71

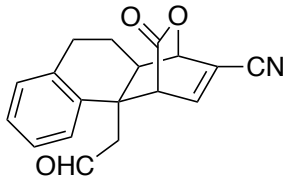
(m, 2 H), 7.67–7.60 (m, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 6.92 (d, *J* = 2.0 Hz, 1 H), 5.61 (t, *J* = 2.0 Hz, 1 H), 3.02 (dd, *J* = 15.8, 2.5 Hz, 1 H), 2.58 (ddd, *J* = 8.9, 4.8, 1.8 Hz, 1 H), 2.49 (dd, *J* = 15.8, 2.1 Hz, 1 H), 2.33 (ddd, *J* = 13.3, 8.9, 7.4 Hz, 1 H), 2.07–1.74 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.61, 189.51, 167.09, 144.78, 142.89, 135.41, 133.84, 129.38, 129.08, 77.93, 70.06, 56.22, 53.00, 49.81, 35.63, 30.36, 26.65; HRMS (ESI) calcd for $C_{19}H_{16}BrO_3^+$ $[M + H - H_2O]^+$ 371.0277, found 371.0278. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 27.80 min (minor), R_t = 31.79 min (major), 78% *ee*.



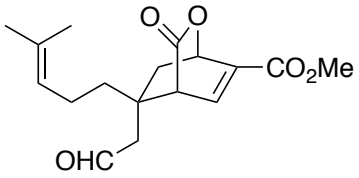
methyl (3a*R*,4*S*,7*R*,7a*R*)-8-oxo-7a-(2-oxoethyl)-1,2,3,3a,4,7a-hexahydro-7*H*-4,7-(epoxymethano)indene-7-carboxylate (*Endo*-47): Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 2:1) to afford the desired product (32.7 mg combined, 56% combined yield; 31.5 mg, 51% yield ***Endo*-47**; 1.5 mg, 5% yield ***Exo*-47**) as a colorless oil. The *dr* was 10.6:1 as determined by crude ^{1}H NMR. ***Endo*-47**: R_f = 0.43 (silica gel, hexanes/EtOAc, 3:2); $[\alpha]_D^{21}$ = +5.72° (*c* = 1.0 in $CHCl_3$); IR (thin film) 3086, 2957, 2875, 2749, 2256, 1754, 1741, 1621, 1278, 1083 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.71 (t, *J* = 3.1 Hz, 1H), 6.72 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.62 (dd, *J* = 7.8, 5.0 Hz, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 3.88 (s, 3H), 2.55 (dd, *J* = 14.0, 3.3 Hz, 1H), 2.39 (dd, *J* = 13.9, 2.8 Hz, 1H), 2.30 (t, *J* = 7.6 Hz, 1H), 2.19 – 2.11 (m, 1H), 2.11 – 1.95 (m, 2H), 1.91 (dh, *J* = 13.3, 3.0 Hz, 1H), 1.80 – 1.65 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.79, 169.48, 168.16, 132.80, 132.18, 78.11, 63.43, 53.15, 51.85, 51.30, 50.36, 36.47, 28.51, 27.61; HRMS (ESI) calcd for C14H15O4$^+$ $[M + H - H_2O]^+$ 247.0971, found 247.0973. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 240 nm) R_t = 22.45 min (minor), R_t = 25.49 min (major), 61% *ee*.



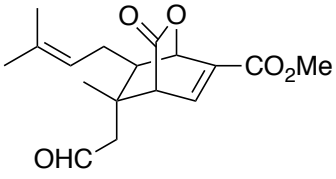
(1*R*,4*R*,8*R*)-3-oxo-8-(2-oxoethyl)-8-phenyl-2-oxabicyclo[2.2.2]oct-5-ene-6-carbonitrile (*Endo*-51): Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (62.4 mg combined, 78% combined yield; 53.0 mg, 66% yield ***Endo*-51**; 9.4 mg, 12% yield ***Exo*-51**) as a colorless oil. The *dr* was 5.5:1 as determined by crude ^{1}H NMR. ***Endo*-51**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –48.90° (*c* = 0.2 in $CHCl_3$); IR (thin film) 2925, 2853, 2225, 1766, 1721, 1585, 1367, 1010 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (t, *J* = 1.8 Hz, 1 H), 7.43–7.36 (m, 5 H), 7.32–7.28 (m, 1 H), 5.41 (dt, *J* = 4.1, 2.0 Hz, 1 H), 4.37 (d, *J* = 6.7 Hz, 1 H), 3.08 (dd, *J* = 14.4, 4.0 Hz, 1 H), 2.83 (dd, *J* = 15.9, 1.6 Hz, 1 H), 2.77 (dd, *J* = 15.9, 2.3 Hz, 1 H), 2.17 (dd, *J* = 14.4, 1.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.23, 168.28, 146.27, 141.56, 129.40, 128.18, 126.68, 118.60, 113.70, 74.68, 54.91, 50.55, 42.94, 39.73; HRMS (ESI) calcd for $C_{16}H_{15}NO_3Na_3^+$ $[M + 3Na]^+$ 112.0196, found 112.0202. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 20.43 min (minor), R_t = 25.78 min (major), 82% *ee*.



(1*R*, 4*R*, 4a*S*, 10a*R*)-11-oxo-4a-(2-oxoethyl)-1, 4, 4a, 9, 10, 10a-hexahydro-1, 4-(epoxymethano)phenanthrene-2-carbonitrile (*Endo*-50): Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 2:1) to afford the desired product (43.0 mg combined, 75% combined yield; 38.7 mg, 68% yield ***Endo*-50**; 4.3 mg, 7% yield ***Exo*-50**) as a pale yellow oil. The *dr* was 8.9:1 as determined by crude ^{1}H NMR. ***Endo*-50**: R_f = 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –117.48° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2941, 2853, 2224, 1769, 1720, 1657, 1588, 736 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 2.5 Hz, 1 H), 7.44 (d, *J* = 7.9 Hz, 1 H), 7.33 (dd, *J* = 6.6, 2.3 Hz, 1 H), 7.31–7.26 (m, 1 H), 7.22 (t, *J* = 7.4 Hz, 1 H), 7.18 (d, *J* = 7.5 Hz, 1 H), 5.15 (d, *J* = 2.3 Hz, 1 H), 4.32 (d, *J* = 6.4 Hz, 1 H), 2.87 (ddd, *J* = 15.7, 6.7, 3.9 Hz, 1 H), 2.73–2.63 (m, 2 H), 2.50 (dd, *J* = 14.3, 2.7 Hz, 1 H), 2.29–2.18 (m, 2 H), 1.82 (qd, *J* = 11.8, 11.3, 7.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.92, 167.92, 145.09, 138.80, 135.32, 129.63, 128.11, 127.74, 126.38, 119.19, 113.76, 79.36, 55.35, 51.86, 44.43, 40.58, 28.18, 26.32; HRMS (ESI) calcd for $C_{54}H_{45}N_3O_9^+$ $[3M]^+$ 879.3156, found 879.3154. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak IA column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 254 nm) R_t = 17.53 min (minor), R_t = 21.06 min (major), 97% *ee*.



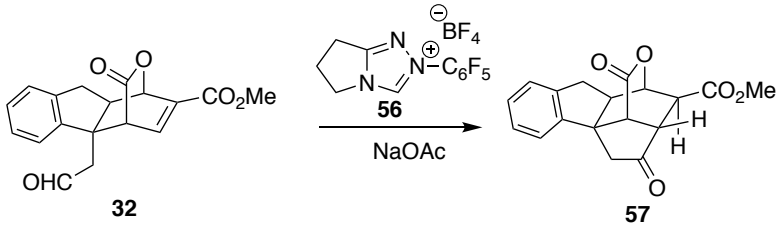
Methyl (1*R*,4*R*,8*S*)-8-(4-methylpent-3-en-1-yl)-3-oxo-8-(2-oxo ethyl)-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (*Endo*-54). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (12.8 mg, 11% yield ***Endo*-54**) as a colorless oil. The *dr* was >20:1 as determined by crude ^{1}H NMR. ***Endo*-54**: R_f= 0.20 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –36.94° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2923, 2857, 1761, 1719, 1636, 1266, 1007 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (t, *J* = 1.8 Hz, 1 H), 7.30 (dd, *J* = 6.5, 2.3 Hz, 1 H), 5.63 (dd, *J* = 4.0, 1.9 Hz, 1 H), 5.03 (tdd, *J* = 5.7, 2.9, 1.4 Hz, 1 H), 3.81 (s, 3 H), 3.77 (d, *J* = 6.5 Hz, 1 H), 2.45 (dd, *J* = 16.6, 1.8 Hz, 1 H), 2.40 (dd, *J* = 16.6, 2.0 Hz, 1 H), 2.17 (dd, *J* = 14.1, 4.0 Hz, 1 H), 2.16–2.06 (m, 1 H), 1.95 (tt, *J* = 13.6, 6.5 Hz, 1 H), 1.72–1.67 (m, 3 H), 1.66 (s, 3 H), 1.58 (d, *J* = 1.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.55, 170.97, 162.51, 140.35, 136.74, 133.11, 122.62, 73.69, 52.46, 51.13, 49.56, 39.46, 39.03, 38.71, 25.73, 23.29, 17.76; HRMS (ESI) calcd for $C_{17}H_{23}O_5^+$ $[M + H]^+$ 307.1540, found 307.1550. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 95:5, flow rate of 1.0 mL/min, 254 nm) R_t = 16.49 min (minor), R_t = 27.44 min (major), 95% *ee*.



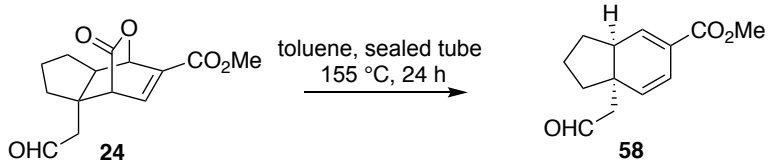
Methyl (1*R*,4*R*,7*R*,8*R*)-8-methyl-7-(3-methylbut-2-en-1-yl)-3-oxo -8-(2-oxoethyl)-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (*Endo* -55). Prepared following the general procedure described above, the crude material was purified by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) to afford the desired product (58.0 mg, 48% yield ***Endo*-55**) as a colorless oil. The *dr* was >20:1 as determined by crude ^{1}H NMR. ***Endo*-55**: R_f= 0.10 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{21}$ = –32.10° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2970, 2855, 1761, 1721, 1439, 1258 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ

9.72 (t, J = 1.8 Hz, 1 H), 7.24 (dd, J = 6.4, 2.3 Hz, 1 H), 5.43 (dd, J = 2.3, 1.1 Hz, 1 H), 5.12 (dddd, J = 7.4, 6.0, 3.0, 1.6 Hz, 1 H), 3.80 (s, 3 H), 3.45 (d, J = 6.3 Hz, 1 H), 2.40 (dd, J = 16.3, 1.8 Hz, 1 H), 2.37–2.30 (m, 2 H), 2.19 (ddd, J = 14.3, 11.2, 8.5 Hz, 1 H), 1.76 (s, 3 H), 1.66 (s, 3 H), 1.51 (ddd, J = 11.2, 4.5, 1.1 Hz, 1 H), 1.28 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.73, 171.34, 162.54, 139.24, 137.43, 135.73, 121.10, 76.15, 55.56, 54.37, 52.42, 45.92, 37.09, 26.65, 25.99, 22.22, 18.08; HRMS (ESI) calcd for $C_{17}H_{23}O_5^+$ $[M + H]^+$ 307.1540, found 307.1530. The enantiomeric excess of its homologated methyl ester was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 97:3, flow rate of 1.0 mL/min, 254 nm) R_t = 18.17 min (minor), R_t = 20.97 min (major), 97% *ee*.

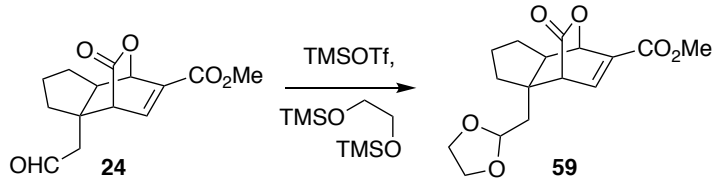
F. Derivatization of Cycloadducts



***tert*-Butyl 3-(8- (methoxycarbonyl)-1, 6-dioxohexahydro- 3, 7- methanocyclopenta[*c*]pyran-4a(1*H*)-yl)-1*H*-indole-1-carboxylate (57).** To a solution of ***Endo*-32** (10.0 mg, 0.023 mmol, 1.0 equiv) in $CHCl_3$ (1.0 mL) at 23 °C was added 6,7-dihydro-2-pentafluorophenyl-5*H*-pyrrolo[2,1-*c*]-1,2,4-triazolium tetrafluoroborate (1.7 mg, 0.0046 mmol, 0.2 equiv) and NaOAc (2.3 mg, 0.028 mmol, 1.2 equiv). The reaction mixture was then warmed to 40 °C and stirred at that temperature for 30 min. Upon completion, the reaction contents were cooled and purified directly by flash column chromatography (silica gel, hexanes/EtOAc, 2:1) to afford the desired cyclized product (9.1 mg, 91% yield) as a yellow oil. **57**: R_f = 0.45 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = –96.80° (c = 0.5 in $CHCl_3$); IR (thin film) 2922, 2850, 1754, 1171 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2 H), 7.26–7.21 (m, 2 H), 5.08 (t, J = 2.2 Hz, 1 H), 3.79 (s, 3 H), 3.50 (d, J = 5.3 Hz, 1 H), 3.37 (dd, J = 17.1, 10.5 Hz, 1 H), 3.26 (d, J = 5.4 Hz, 2 H), 3.26 (d, J = 17.0, 5.9 Hz, 2 H), 2.93–2.90 (m, 1 H), 2.85 (dd, J = 18.3, 1.5 Hz, 1 H), 2.63 (d, J = 18.3 Hz, 1 H), 2.62–2.59 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.78, 170.25, 169.42, 141.76, 140.40, 129.17, 127.93, 125.53, 123.02, 77.85, 56.05, 53.37, 51.66, 49.78, 48.13, 48.11, 47.32, 34.07; HRMS (ESI) calcd for $C_{36}H_{33}O_{10}^+$ $[2M + H]^+$ 625.2069, found 625.206. The enantiomeric excess was determined by chiral HPLC using a Daicel Chiralpak OD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 205 nm) R_t = 49.45 min (major), R_t = 74.00 min (minor), 96% *ee*.

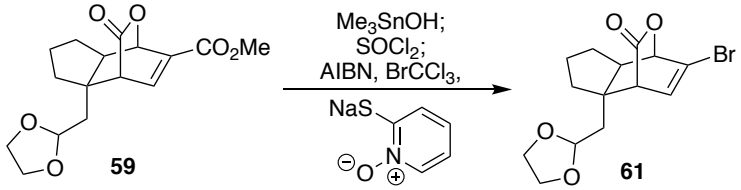


Methyl (3a*S*, 7a*S*)-7a-(2 -oxoethyl)-2, 3, 3a ,7a-tetrahydro-1*H*-indene-5-carboxylate (58). To a 5 mL sealed tube was added a solution of ***Endo*-24** (19.8 mg, 0.075 mmol, 1.0 equiv) in toluene (1.5 mL) and the contents heated at 155 °C for 24 h. Upon completion, the reaction mixture was cooled to 23 °C and concentrated directly. Purification of the resultant crude product by flash column chromatography (silica gel, hexanes/EtOAc, 3:1) gave the desired product retro Diels–Alder product (5.5 mg, 67% yield) as a yellow oil. Following the general procedure delineated above, aldehyde **58** was converted into the corresponding homologated α,β-unsaturated ester for HPLC analysis. **58**: R_f = 0.78 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = +52.6° (*c* = 1.0 in $CHCl_3$); IR (thin film) 2951, 2928, 2869, 2862, 1719, 1654, 1263, 1090 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.61 (t, *J* = 2.8 Hz, 1 H), 7.02 (d, *J* = 5.6 Hz, 1 H), 6.38 (dd, *J* = 9.9, 1.5 Hz, 1 H), 5.67 (d, *J* = 9.8 Hz, 1 H), 3.77 (s, 3 H), 2.50 (td, *J* = 8.5, 7.9, 5.5 Hz, 1 H), 2.39 (d, *J* = 2.9 Hz, 2 H), 2.19–2.06 (m, 1 H), 1.94–1.78 (m, 2 H), 1.56–1.43 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.15, 166.31, 139.99, 133.22, 125.38, 119.96, 54.92, 51.93, 44.51, 41.37, 34.55, 29.86, 22.80; HRMS (ESI) calcd for $C_{13}H_{17}O_3^+$ $[M + H]^+$ 221.1172, found 221.1163. The enantiomeric excess was determined by chiral HPLC using a Daicel Chiralpak OJ-H column (hexanes/*i*PrOH, 99:1, flow rate of 1.0 mL/min, 215 nm) R_t = 14.70 min (minor), R_t = 17.68 min (major), 96% *ee*.



Methyl (3a*R*,4*R*,7*R*,7a*R*)-7a-((1,3-dioxolan-2-yl)methyl)-8-oxo-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-(epoxymethano)indene-5-carboxylate (59). To a solution of ***Endo*-24** (19.8 mg, 0.075 mmol, 1.0 equiv) in CH_2Cl_2 (1.5 mL) at 0 °C was added bis(trimethylsiloxy)ethane (0.037 mL, 0.15 mmol, 2.0 equiv) and TMSOTf (0.002 mL, 0.0075 mmol, 0.1 equiv). The resultant solution was stirred at 0 °C for 1 h. Upon completion, the reaction contents were quenched with H_2O (1 mL), poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with CH_2Cl_2 (2 × 2 mL). The combined organic layers were dried (Na_2SO_4), concentrated, purified by filtration through a short silica gel plug (silica gel, hexanes/EtOAc, 1:1) to afford the desired acetal (22.7 mg, 98% yield) as a colorless oil. **59**: R_f = 0.19 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = –26.92° (*c* = 1.0 in $CHCl_3$). IR (thin film) 2954, 2888, 1761, 1717, 1631, 1252 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 6.4, 2.1 Hz, 1 H), 5.43 (s, 1 H), 4.83 (dd, *J* = 6.9, 2.5 Hz, 1 H), 3.99 (q, *J* = 6.5 Hz, 1 H), 3.96–3.89 (m, 1 H), 3.89–3.83 (m, 1 H), 3.81–3.77 (m, 2 H), 3.80 (s, 3 H), 2.00–1.58 (m, 7 H), 1.53 (dd, *J* = 14.4, 6.9 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.83, 163.08, 142.74, 136.10, 102.26, 77.57, 65.25, 64.47, 52.29, 51.59, 50.55, 47.99, 43.91, 35.39, 28.32, 27.33; HRMS (ESI) calcd for $C_{32}H_{41}O_{12}^+$ $[2M + H]^+$ 617.2598, found 617.2607.

Dimethyl (3a*R*,4*R*,7*R*,7a*R*)-3a-((1,3-dioxolan-2-yl)methyl)-7-(benzoyloxy)-2,3,3a,4,7, 7a-hexahydro-1*H*-indene-4,6-dicarboxylate (60). Acetal **59** (9.3 mg, 0.03 mmol, 1.0 equiv) was dissolved in MeOH/CH_2Cl_2 (0.3 mL, 4:1) and cooled to 0 °C. To this solution was then added NaOMe (0.5 M in MeOH, 0.12 mL, 0.06 mmol, 2.0 equiv) dropwise. The resultant reaction mixture was then stirred at 0 °C for 2 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (5 mL), poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Pressing forward without any additional purification, the resultant crude material was then dissolved in CH_2Cl_2 (0.4 mL) and 4-DMAP (4.4 mg, 0.036 mmol, 2.0 equiv), Et_3N (0.005 mL, 0.036 mmol, 2.0 equiv) and benzoyl chloride (0.005 mL, 0.036 mmol, 2.0 equiv) were added sequentially at 23 °C. The resultant reaction mixture was then stirred for 1 h at 23 °C. Upon completion, the reaction mixture was purified directly by preparative TLC (silica gel, hexanes/EtOAc, 3:1) to give the desired product (8.9 mg, 67% yield) as a colorless oil. **60**: R_f = 0.42 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = –22.48° (*c* = 0.5 in $CHCl_3$); IR (thin film) 2952, 2885, 1807, 1715, 1243 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18–8.09 (m, 1 H), 7.67–7.61 (m, 1 H), 7.53–7.47 (m, 2 H), 6.97 (d, *J* = 3.9 Hz, 1 H), 4.89 (dd, *J* = 6.9, 2.8 Hz, 1 H), 4.83 (dd, *J* = 4.0, 1.2 Hz, 1 H), 3.95–3.88 (m, 2 H), 3.85–3.72 (m, 5 H), 3.50 (s, 3 H), 3.30 (d, *J* = 4.1 Hz, 1 H), 2.79 (d, *J* = 8.4 Hz, 1 H), 2.73–2.64 (m, 1 H), 2.20 (dd, *J* = 14.9, 7.0 Hz, 1 H), 2.13–2.03 (m, 1 H), 1.83 (dd, *J* = 14.9, 2.9 Hz, 1 H), 1.78–1.70 (m, 1 H), 1.64 (dt, *J* = 5.5, 2.9 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.08, 166.97, 162.36, 147.30, 134.43, 130.73, 128.90, 103.02, 77.36, 73.65, 65.01, 64.57, 60.01, 52.02, 51.26, 45.81, 42.78, 42.27, 35.54, 31.22, 23.54; HRMS (ESI) calcd for $C_{24}H_{24}O_6^+$ $[M - 2H_2O]^+$ 213.0839, found 213.0840. The enantiomeric excess was determined by chiral HPLC using a Daicel Chiralpak AD-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 240 nm) R_t = 13.57 min (minor), R_t = 15.17 min (major), 95% *ee*.



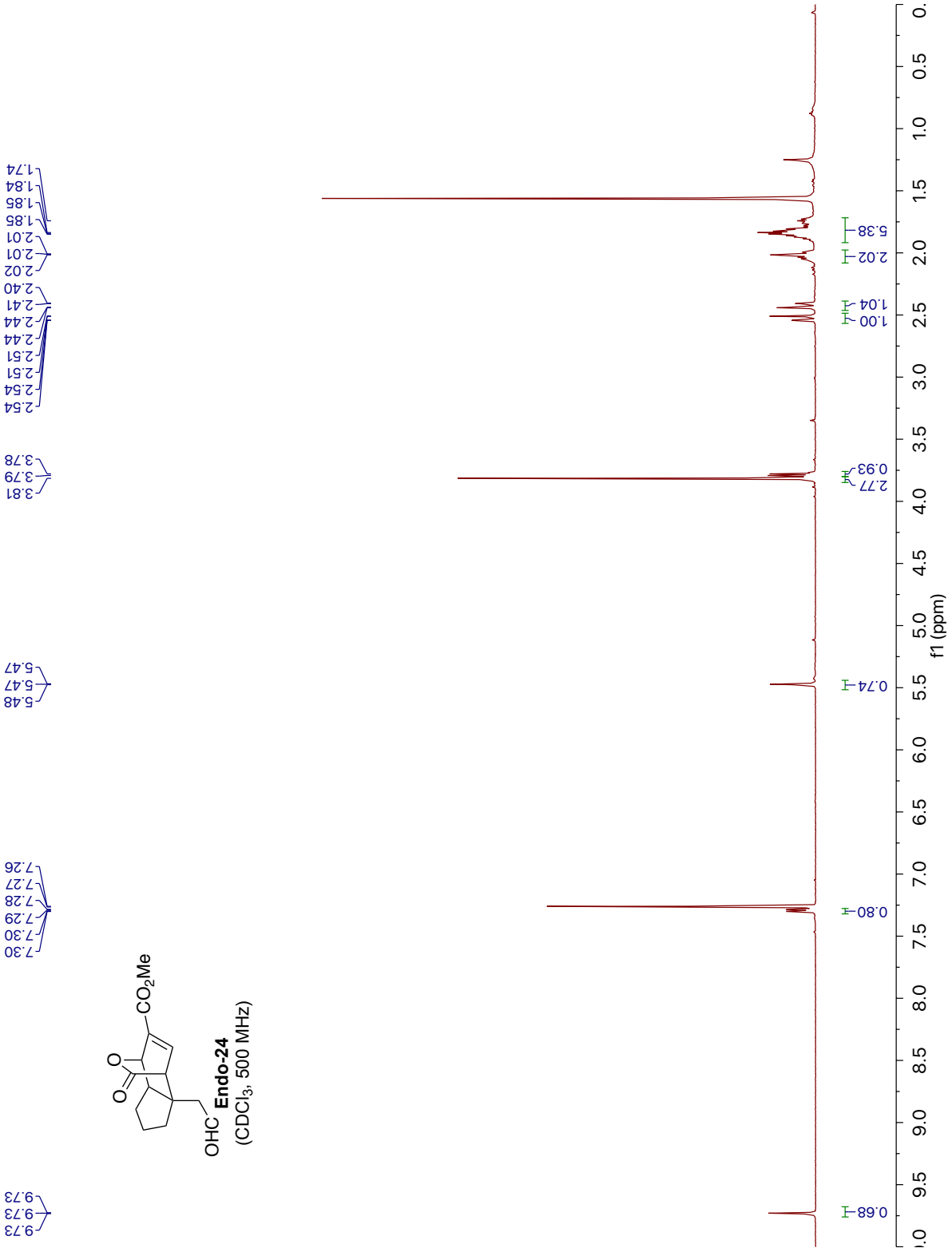
(3a*R*,4*R*,7*R*,7a*R*)-7a-((1,3-dioxolan-2-yl)methyl)-5-Bromo-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-(epoxymethano)inden-8-one (61). To a solution of bicycle **59** (9.3 mg, 0.03 mmol, 1.0 equiv) in $ClCH_2CH_2Cl$ (0.75 mL) at 23 °C was added Me_3SnOH (17.5 mg, 0.09 mmol, 3.0 equiv). The resultant reaction mixture was then heated at 80 °C for 16 h. Upon completion, the reaction contents were cooled and concentrated directly. Pressing forward without any further purification, the resultant crude material was dissolved in toluene (0.35 mL) and then $SOCl_2$ (0.015 mL, 0.17 mmol, 5.0 equiv) was added at 23 °C. The resultant reaction mixture was stirred at 23 °C for 24

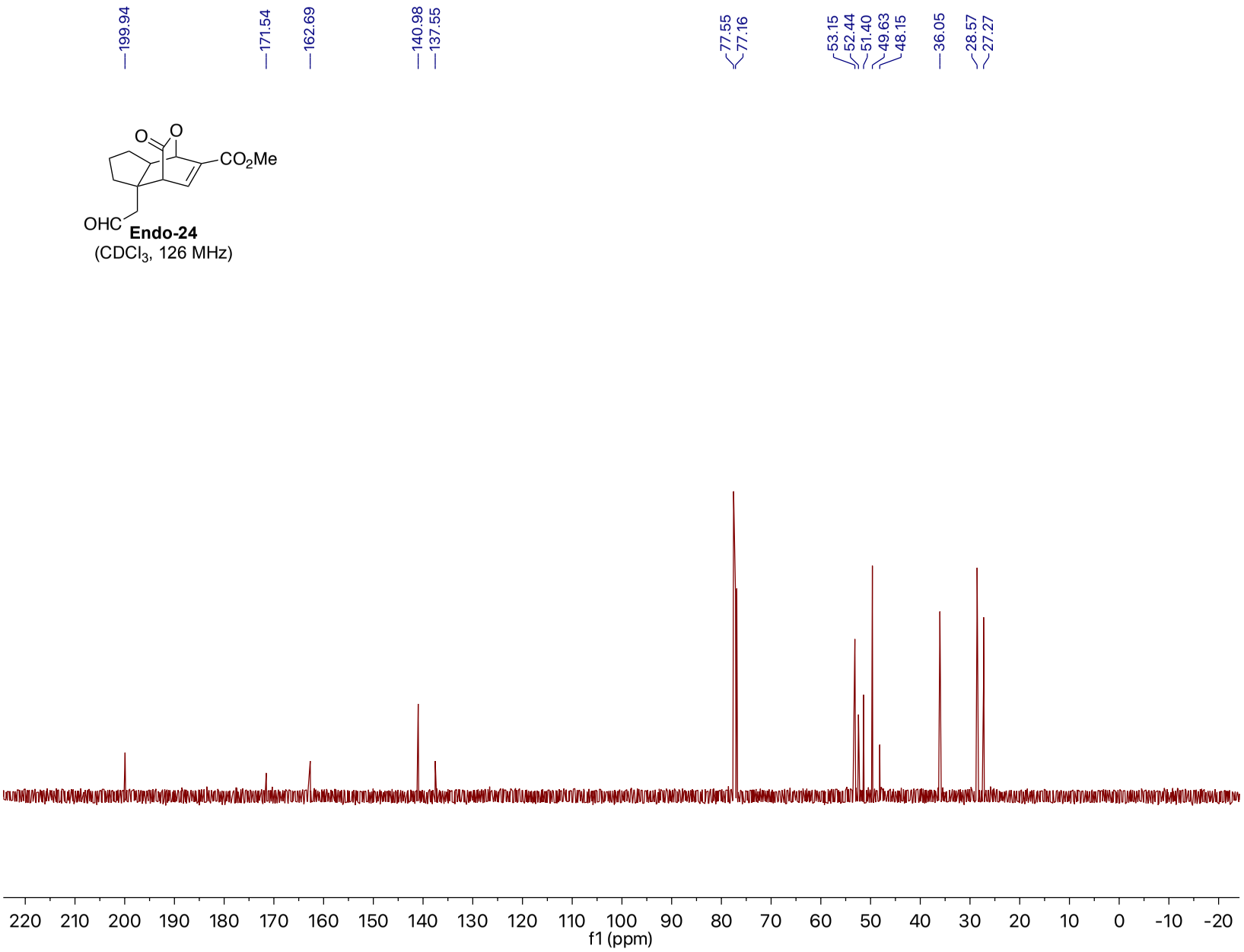
h. Upon completion, the reaction contents were concentrated directly. The resultant crude residue was then dissolved in $BrCCl_3$ (0.3 mL) and AIBN (0.6 mg, 0.0034 mmol, 0.1 equiv) was then added at 23 °C. This mixture was then added via syringe pump to a solution of 2-mercaptopyridine *N*-oxide sodium salt (5.6 mg, 0.037 mmol, 1.1 equiv) in bromotrichloromethane (0.3 mL) at 100 °C over the course of 30 min. Upon completion, the reaction contents were cooled to 23 °C, concentrated, and purified directly by flash column chromatography (silica gel, hexanes/EtOAc, 3:2) to give the desired vinyl bromide (4.3 mg, 38% yield) as a colorless oil. **61:** R_f = 0.35 (silica gel, hexanes/EtOAc, 2:1); $[\alpha]_D^{23}$ = –53.20° (*c* = 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 6.6, 2.4 Hz, 1 H), 4.88–4.79 (m, 2 H), 4.03–3.89 (m, 2 H), 3.89–3.75 (m, 2 H), 3.63 (d, *J* = 6.6 Hz, 1 H), 2.09–2.03 (m, 1 H), 1.96–1.90 (m, 1 H), 1.81 (ddt, *J* = 14.8, 9.9, 3.7 Hz, 3 H), 1.77–1.63 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.49, 121.18, 102.37, 84.74, 65.22, 64.50, 52.51, 50.58, 48.07, 43.59, 35.05, 29.85, 28.33, 27.43; HRMS (ESI) calcd for $C_{28}H_{34}Br_2O_8Na^+$ $[2M + Na]^+$ 679.0518, found 679.0515. The enantiomeric excess was determined by chiral HPLC using a Daicel Chiralpak AS-H column (hexanes/*i*PrOH, 90:10, flow rate of 1.0 mL/min, 215 nm) R_t = 34.66 min (major), R_t = 39.10 min (minor), 92% *ee*.

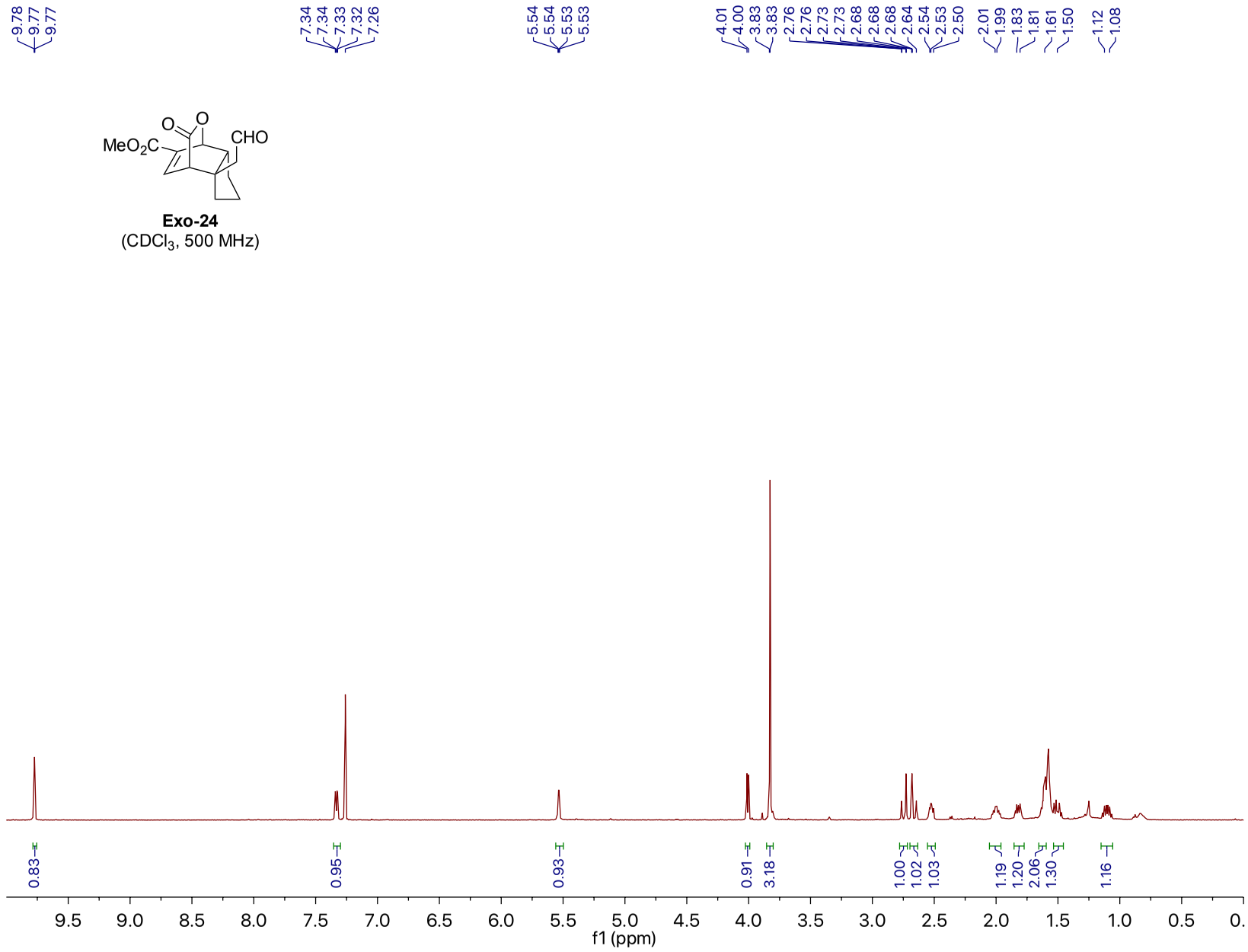
G. References

1. R. L. Snowden, M. Wüst, *Tetrahedron Lett.* **1986**, *27*, 699.
2. S. K. Karagiozov, F. S. Abbott, *Syn. Comm.* **2004**, *34*, 871.
3. M. J. González, J. González, L. A. López, R. Vincente, *Angew. Chem. Int. Ed.* **2015**, *54*, 12139.
4. N. Brindani, G. Rassu, L. Dell'Amico, V. Zambrano, L. Pinna, C. Curti, A. Sartori, L. Battistini, G. Casiraghi, G. Pelosi, *Angew. Chem. Int. Ed.* **2015**, *54*, 7386.
5. Z. Wu, F. Li, J. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 1629.
6. R. H. Wiley, S. Slaymaker, *J. Am. Chem. Soc.* **1956**, *78*, 2393.
7. I. Ashworth, M. Bowden, B. Dembofsky, D. Levin, W. Moss, E. Robinson, N. Szczur, J. Virica, *Org. Proc. Res. Dev.* **2003**, *7*, 74.
8. Y. Hoshino, Y. Ikeda, Y. Nakai, K. Honda, *Chem. Lett.* **2017**, *46*, 1743.

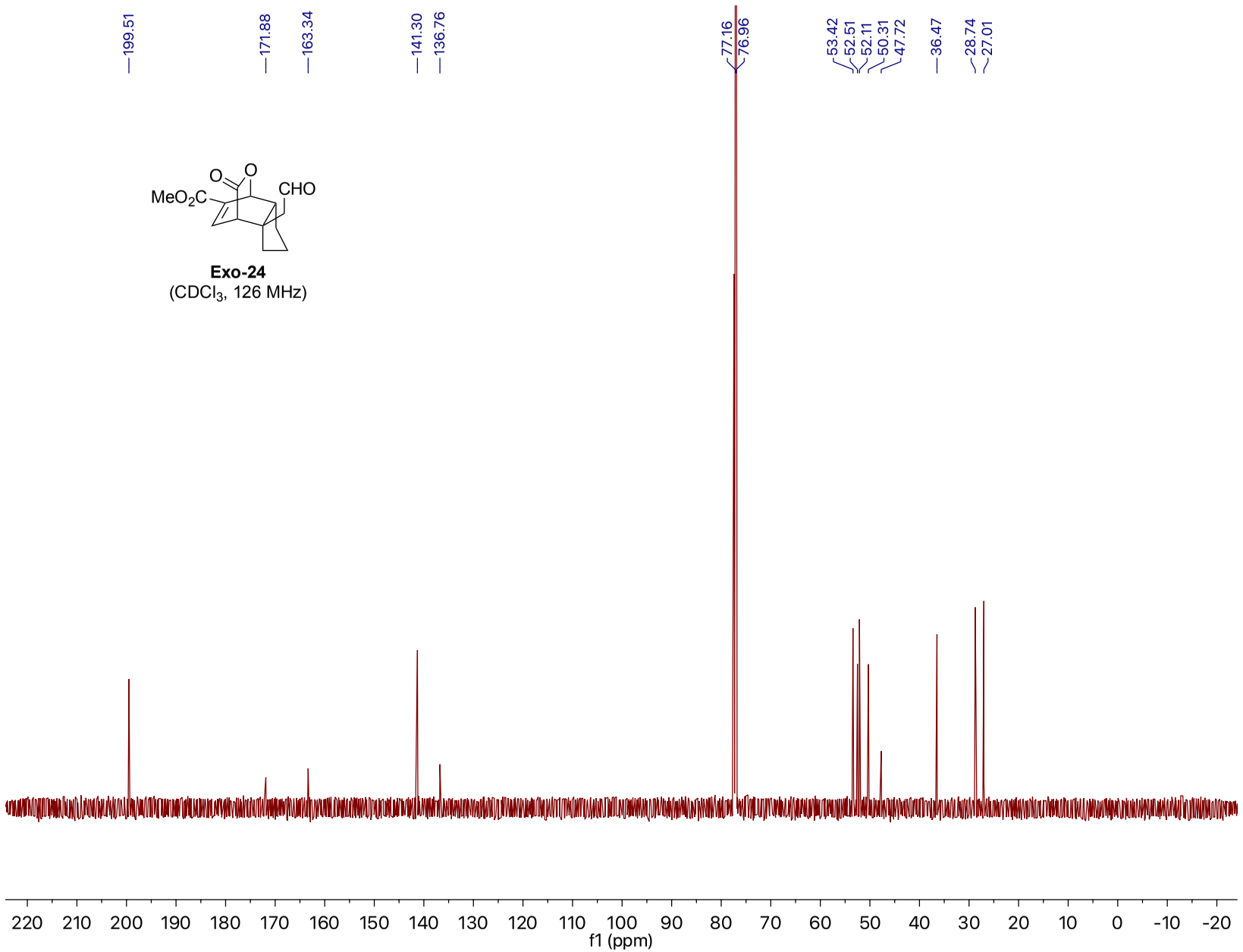
H. ^{1}H and ^{13}C Spectra

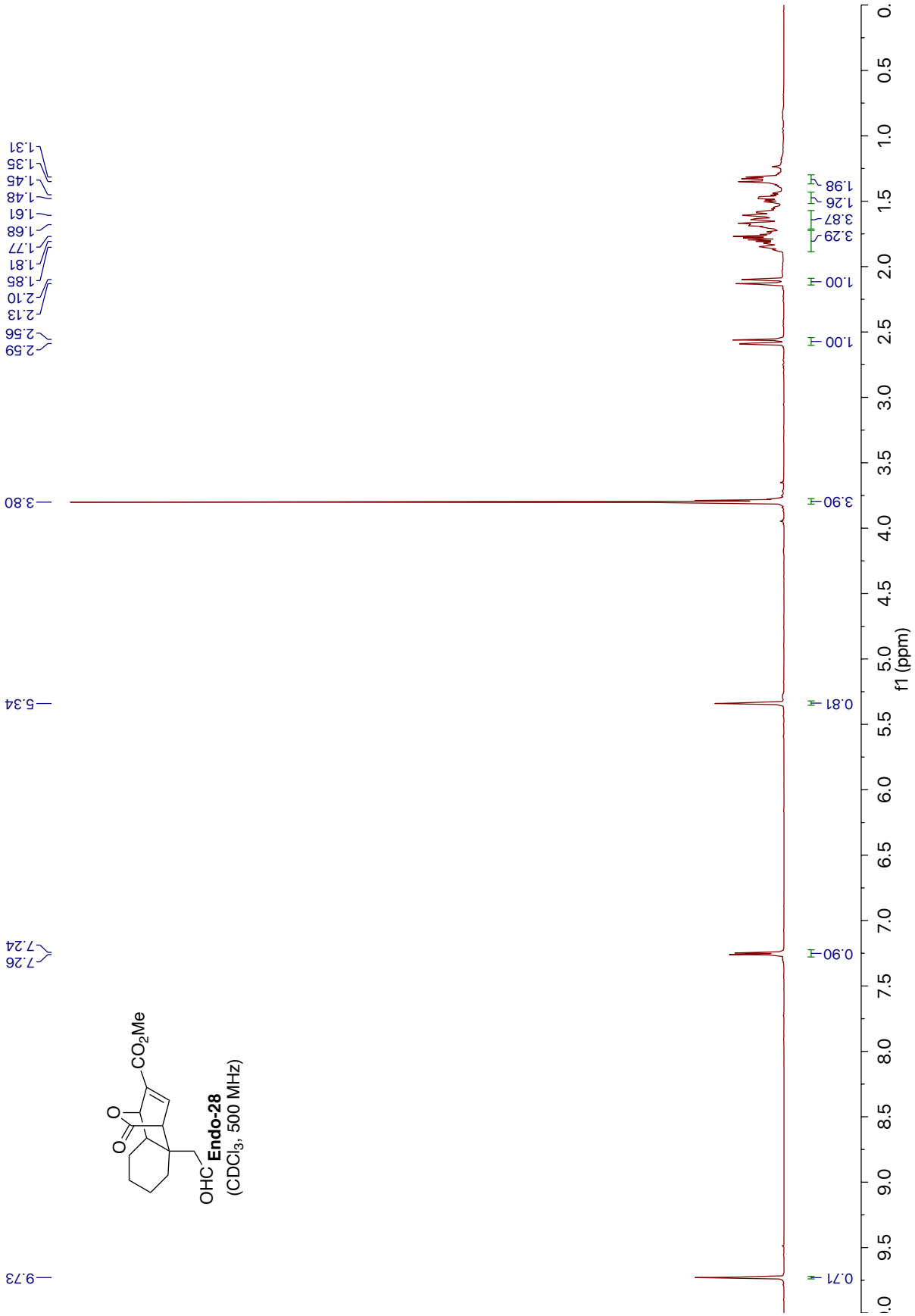


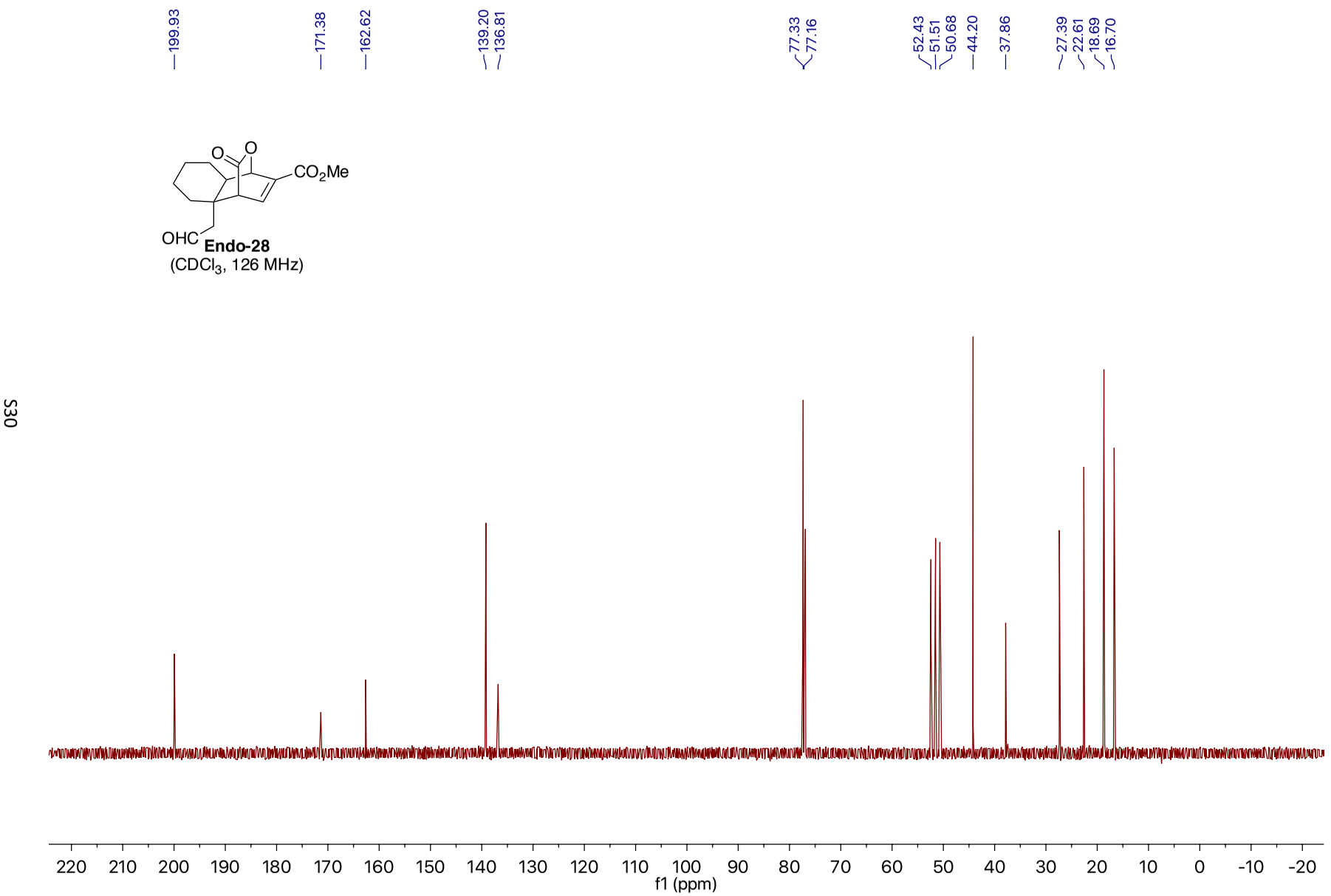

199.94
171.54
162.69
140.98
137.55
77.55
77.16
53.15
52.44
51.40
49.63
48.15
36.05
28.57
27.27
O
O
CO2Me
OHC
Endo-24
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

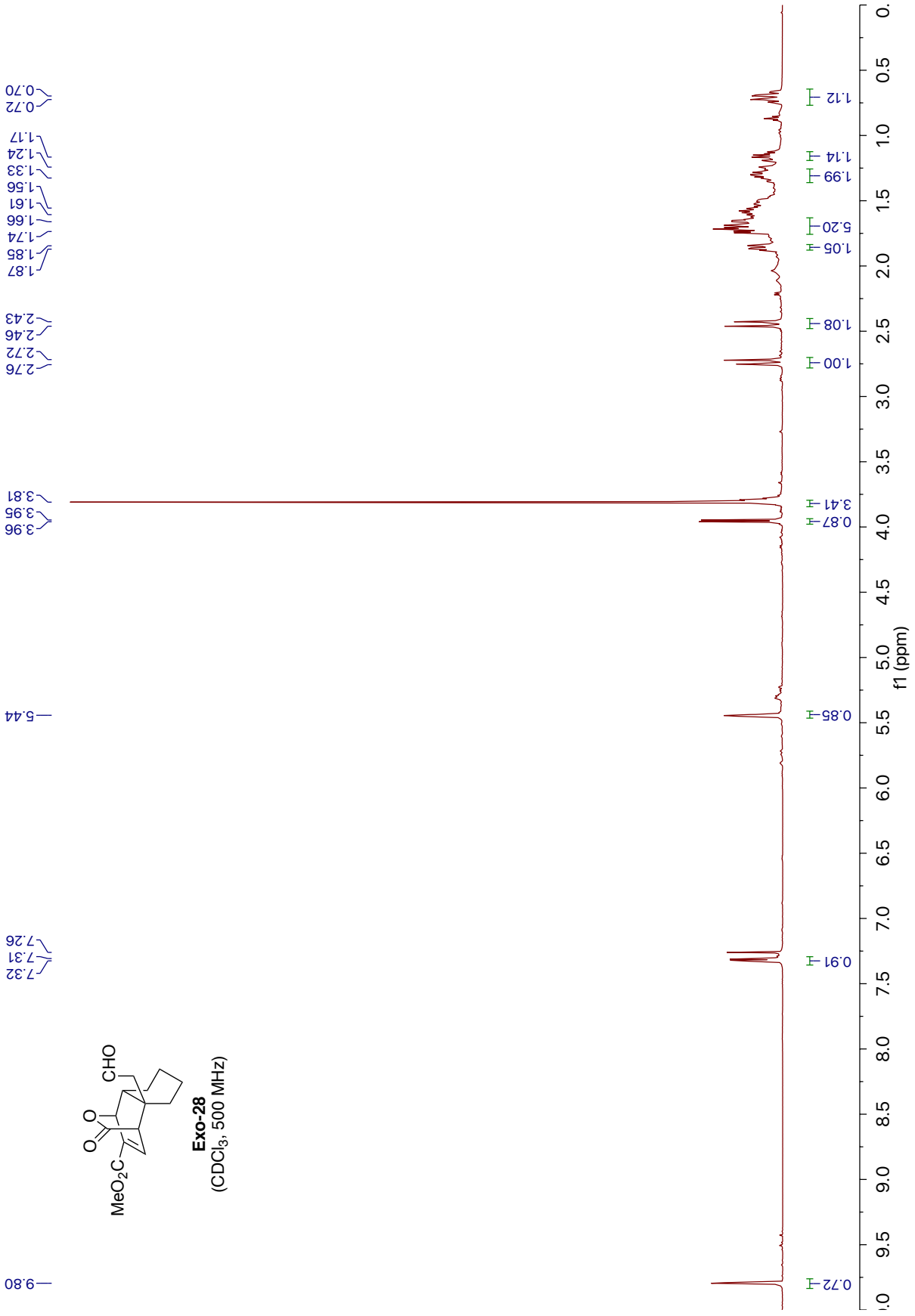


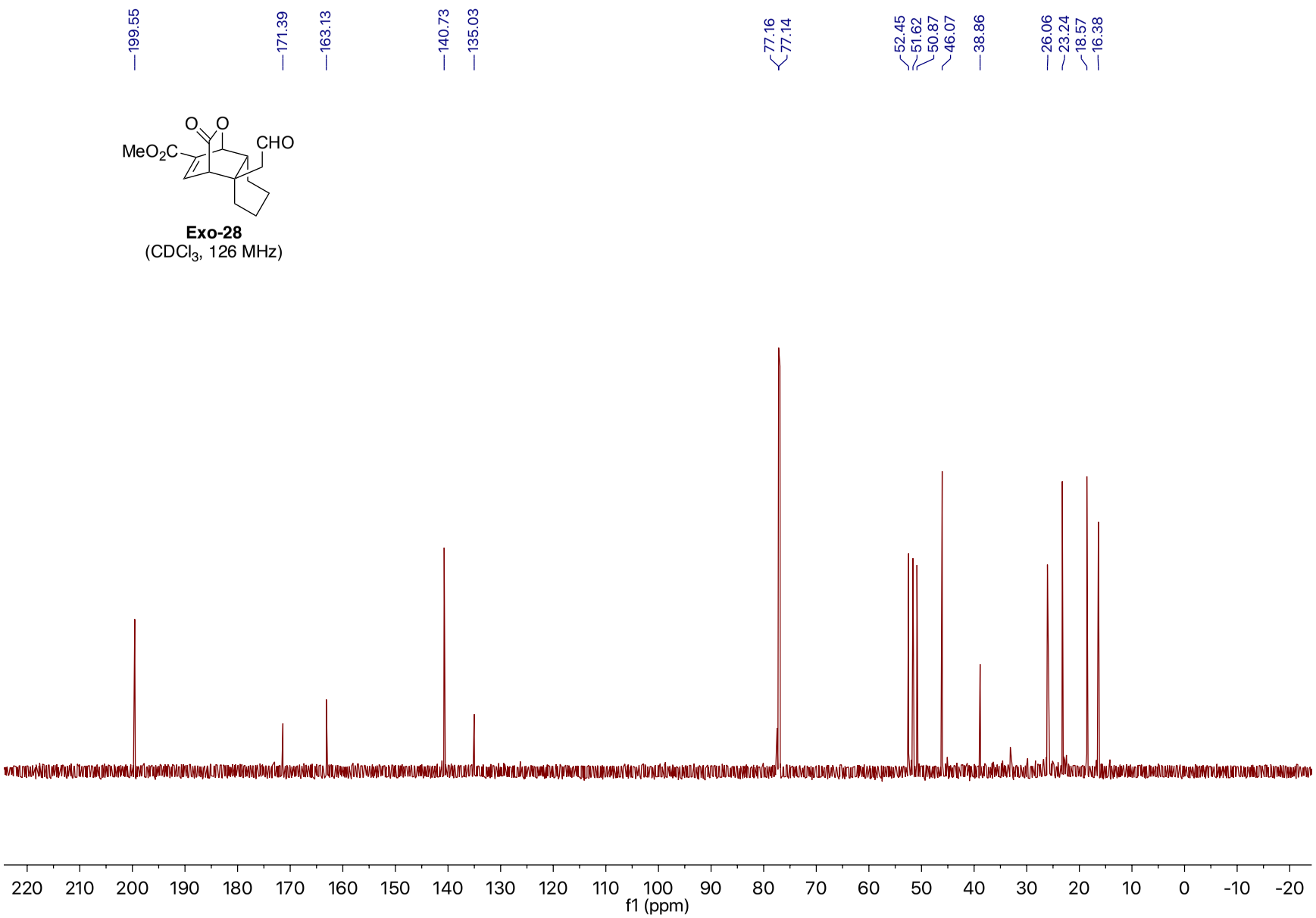
Exo-24
($CDCl_3$, 500 MHz)

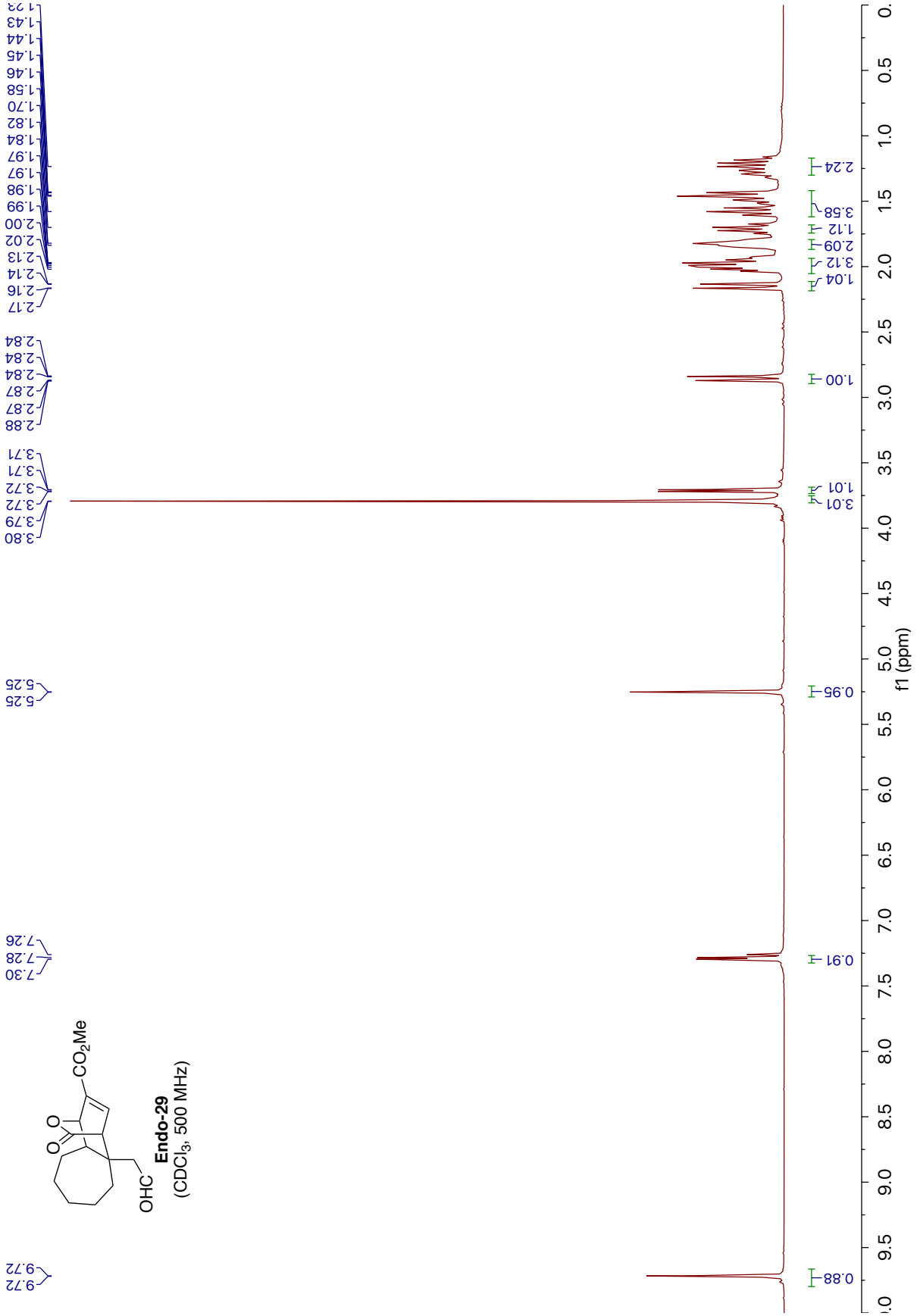

199.51
171.88
163.34
141.30
136.76
77.16
76.96
53.42
52.51
52.11
50.31
47.72
36.47
28.74
27.01
O
O
MeO2C
CHO
Exo-24
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

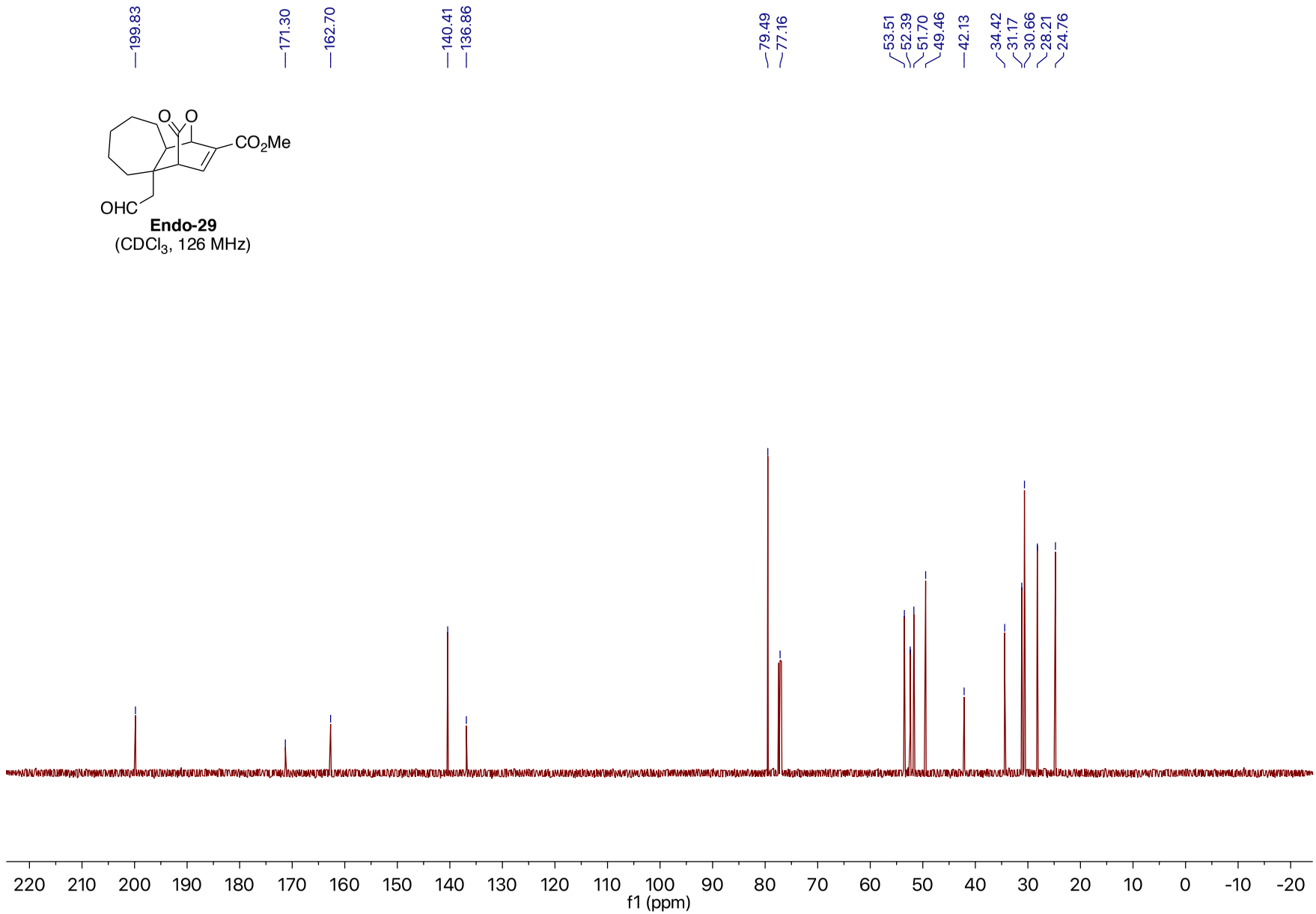

CO2Me
O
O
OHC
Endo-28
(CDCl3, 500 MHz)
9.73
7.26
7.24
5.34
3.80
2.59
2.56
2.13
2.10
1.85
1.81
1.77
1.68
1.61
1.48
1.45
1.35
1.31
0.71
0.90
0.81
3.90
1.00
1.00
3.29
3.87
1.26
1.98
f1 (ppm)

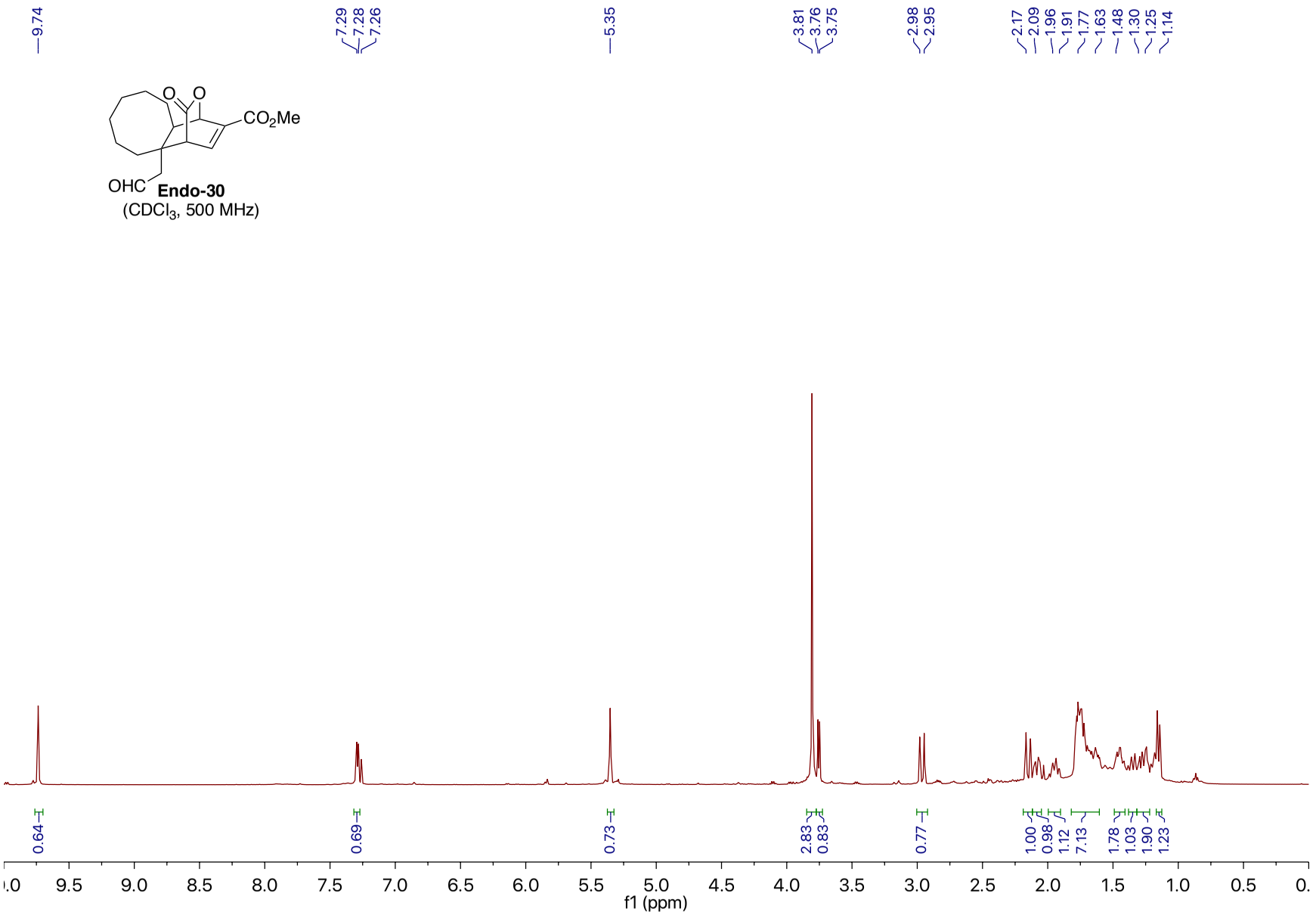

199.93
171.38
162.62
139.20
136.81
77.33
77.16
52.43
51.51
50.68
44.20
37.86
27.39
22.61
18.69
16.70
O
O
CO2Me
OHC
Endo-28
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

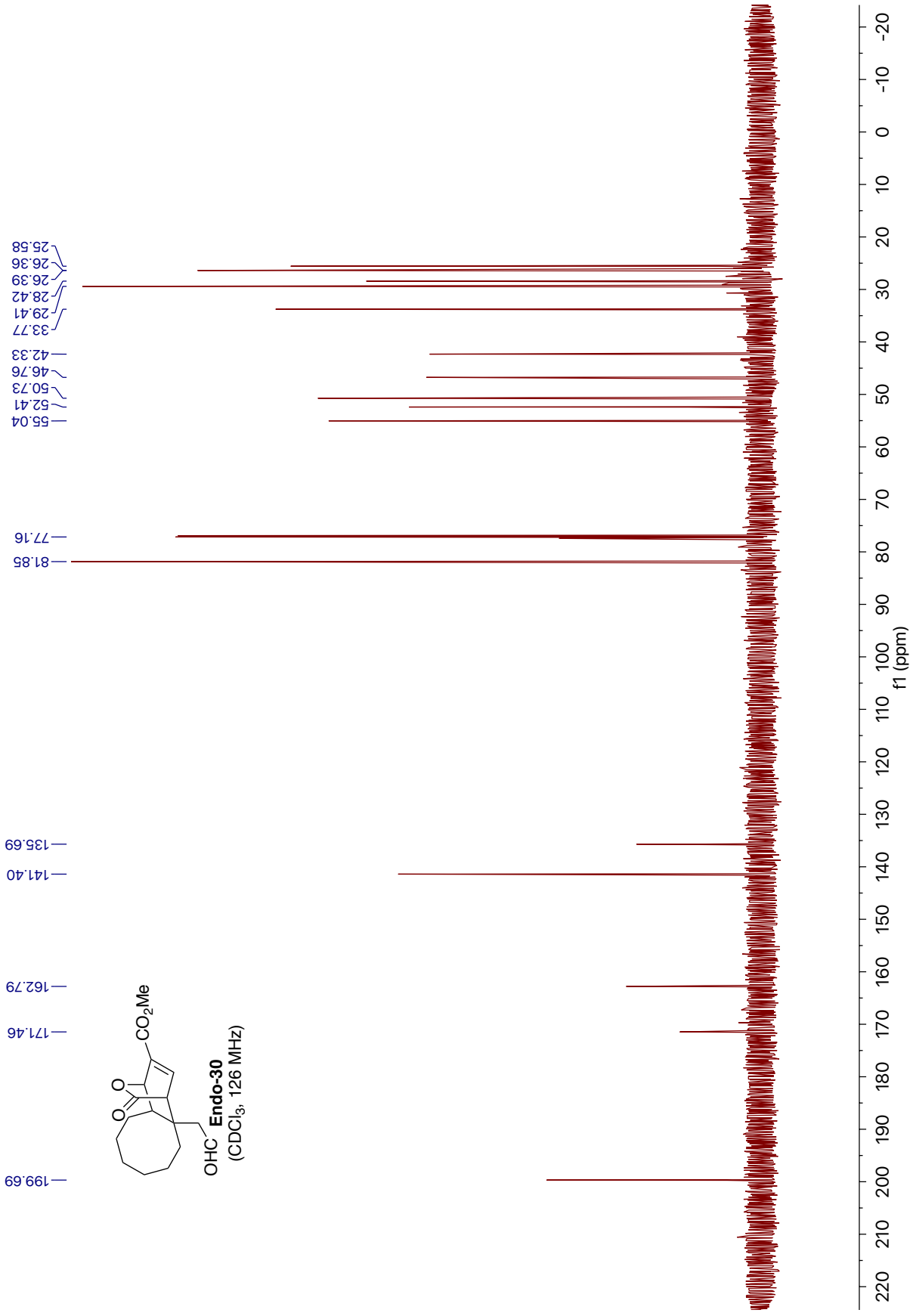

9.80
7.32
7.31
7.26
5.44
3.96
3.95
3.81
2.76
2.72
2.46
2.43
1.87
1.85
1.74
1.66
1.61
1.56
1.33
1.24
1.17
0.72
0.70
0.72
0.91
0.85
3.41
0.87
1.00
1.08
1.05
5.20
1.99
1.14
1.12
f1 (ppm)
CHO
O
O
O
MeO2C
Exo-28
(CDCl3, 500 MHz)

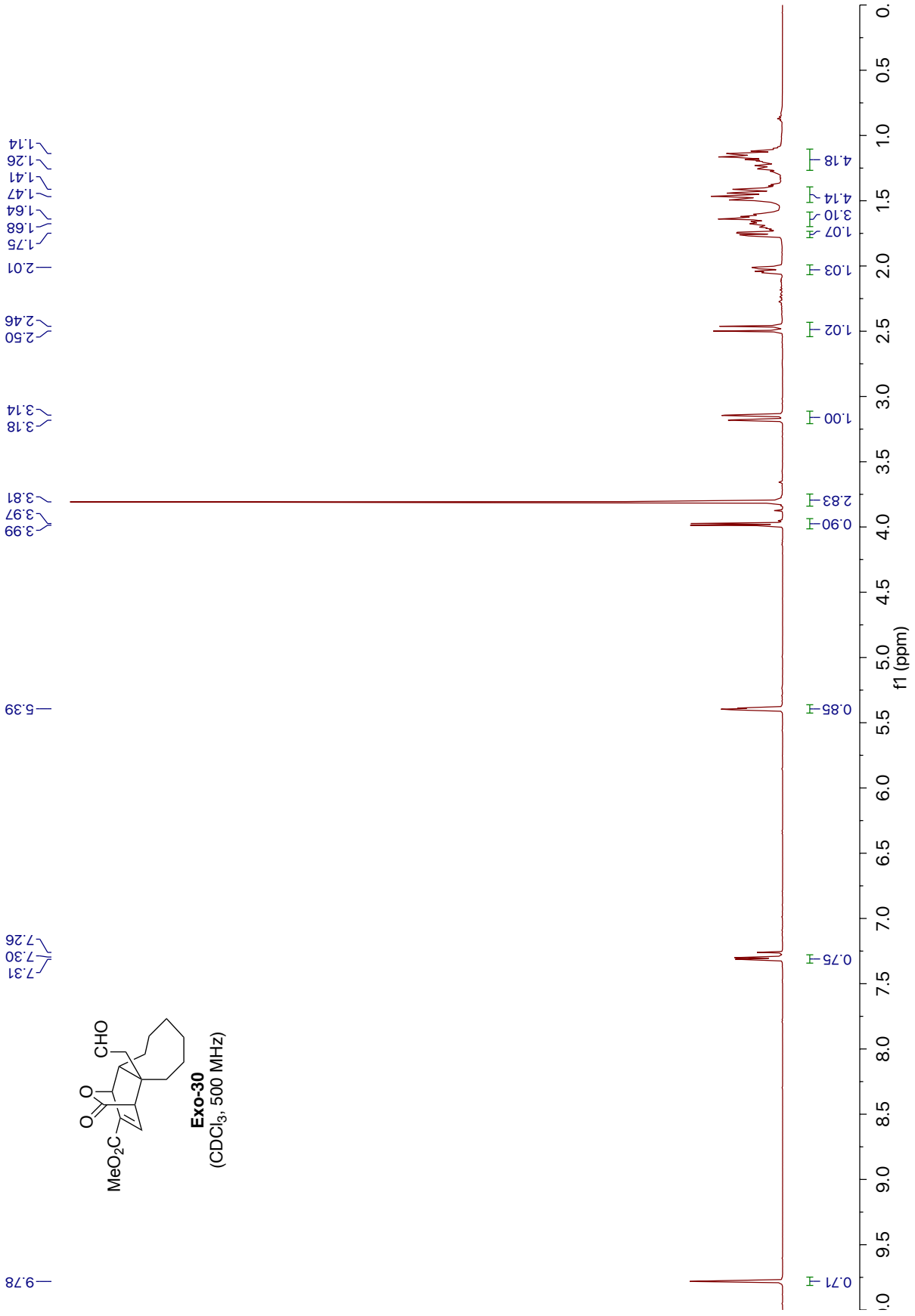

199.55
171.39
163.13
140.73
135.03
77.16
77.14
52.45
51.62
50.87
46.07
38.86
26.06
23.24
18.57
16.38
O
O
MeO2C
CHO
Exo-28
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

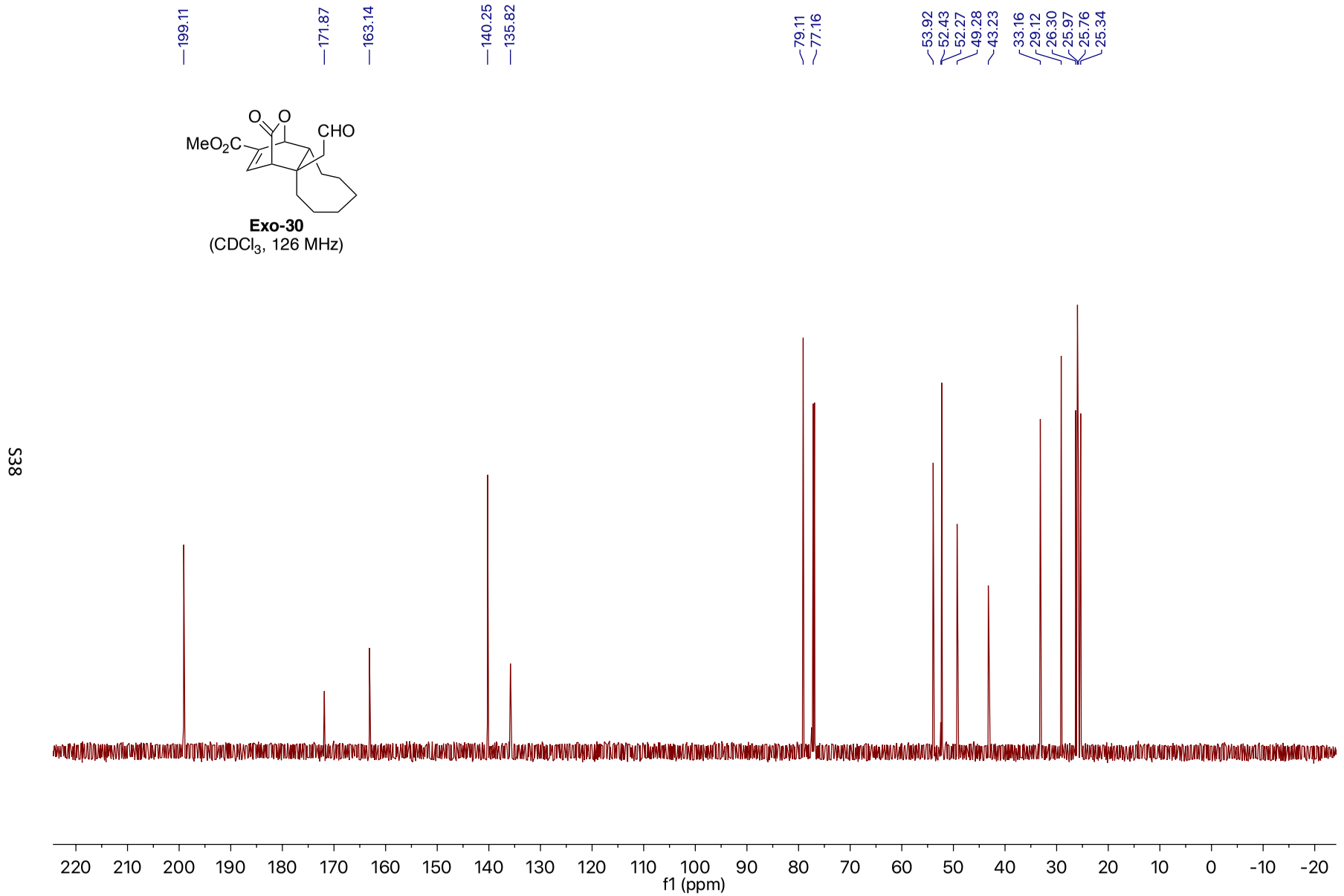

CO2Me
O
O
OHC
Endo-29
(CDCl3, 500 MHz)
f1 (ppm)

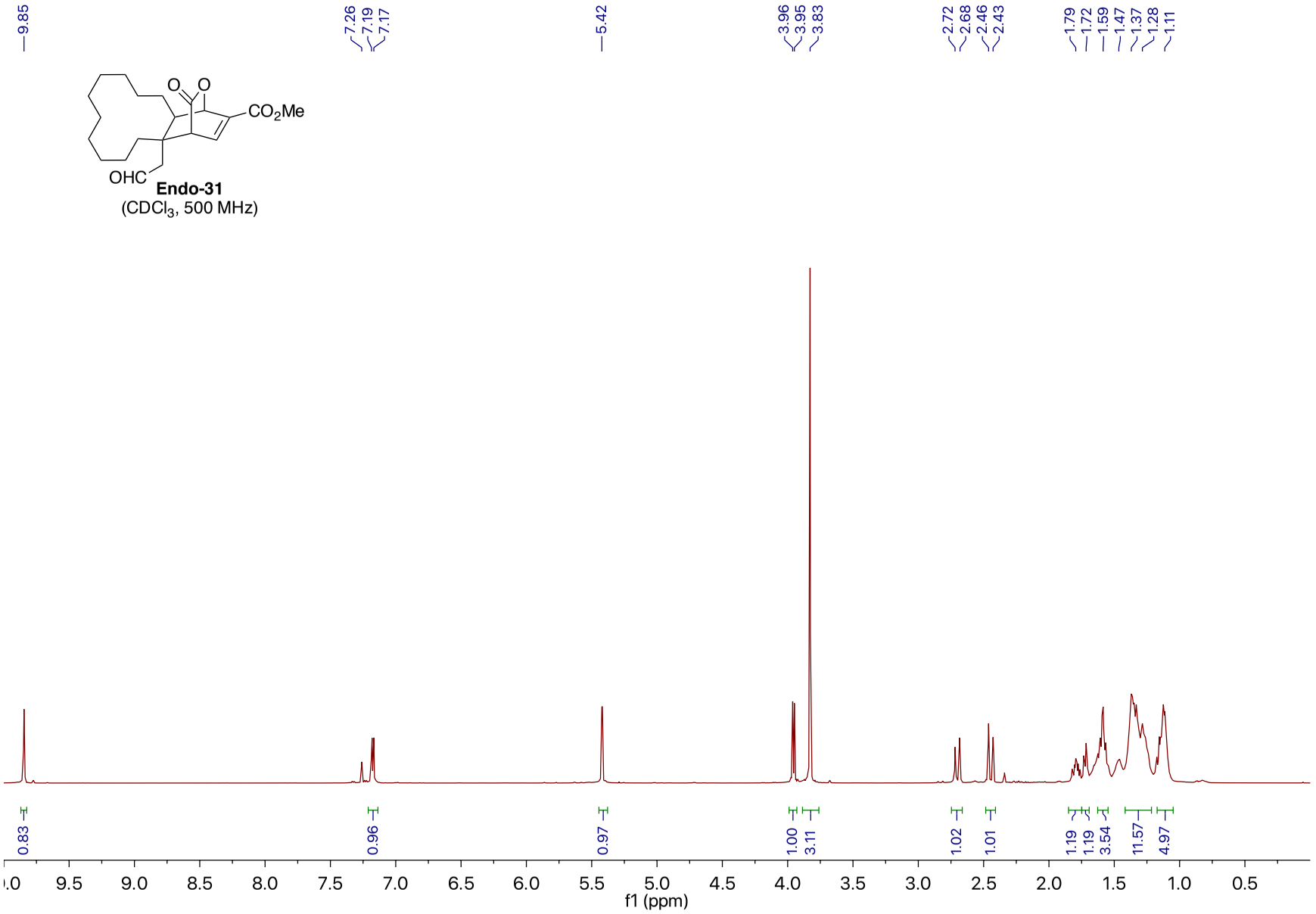

199.83
171.30
162.70
140.41
136.86
79.49
77.16
53.51
52.39
51.70
49.46
42.13
34.42
31.17
30.66
28.21
24.76
O
O
CO2Me
OHC
Endo-29
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


9.74
7.29
7.28
7.26
5.35
3.81
3.76
3.75
2.98
2.95
2.17
2.09
1.96
1.91
1.77
1.63
1.48
1.30
1.25
1.14
O
O
CO2Me
OHC
Endo-30
(CDCl3, 500 MHz)
0.64
0.69
0.73
2.83
0.83
0.77
1.00
0.98
1.12
7.13
1.78
1.03
1.90
1.23
f1 (ppm)

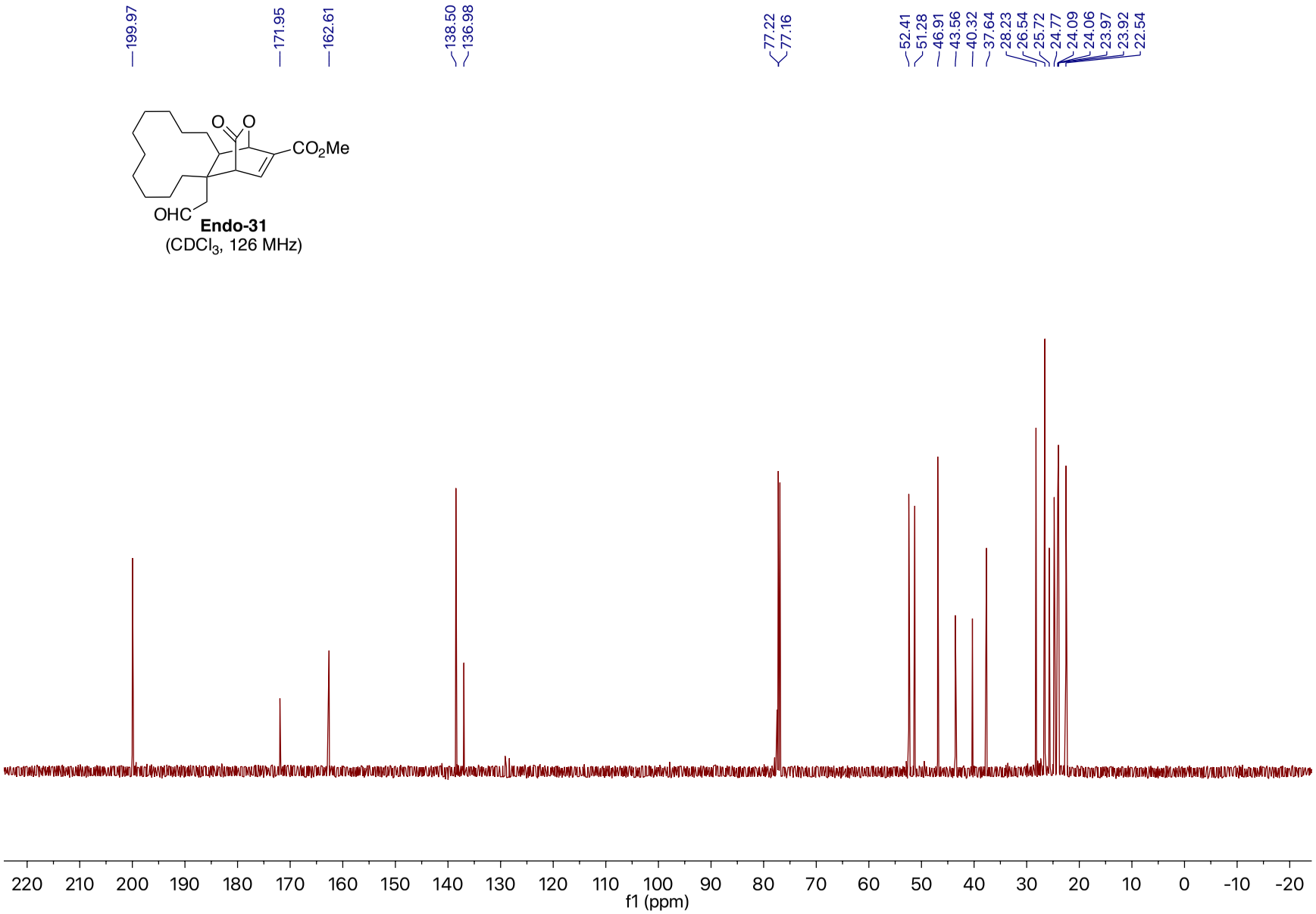

199.69
171.46
162.79
141.40
135.69
81.85
77.16
55.04
52.41
50.73
46.76
42.33
33.77
29.41
28.42
26.39
26.36
25.58
CO2Me
O
O
OHC
Endo-30
(CDCl3, 126 MHz)
f1 (ppm)


CHO
O
O
MeO2C
Exo-30
(CDCl3, 500 MHz)
9.78
7.31
7.30
7.26
5.39
3.99
3.97
3.81
3.18
3.14
2.50
2.46
2.01
1.75
1.68
1.64
1.47
1.41
1.26
1.14
0.71
4.18
4.14
3.10
1.07
1.03
1.02
1.00
2.83
0.90
0.85
0.75
f1 (ppm)

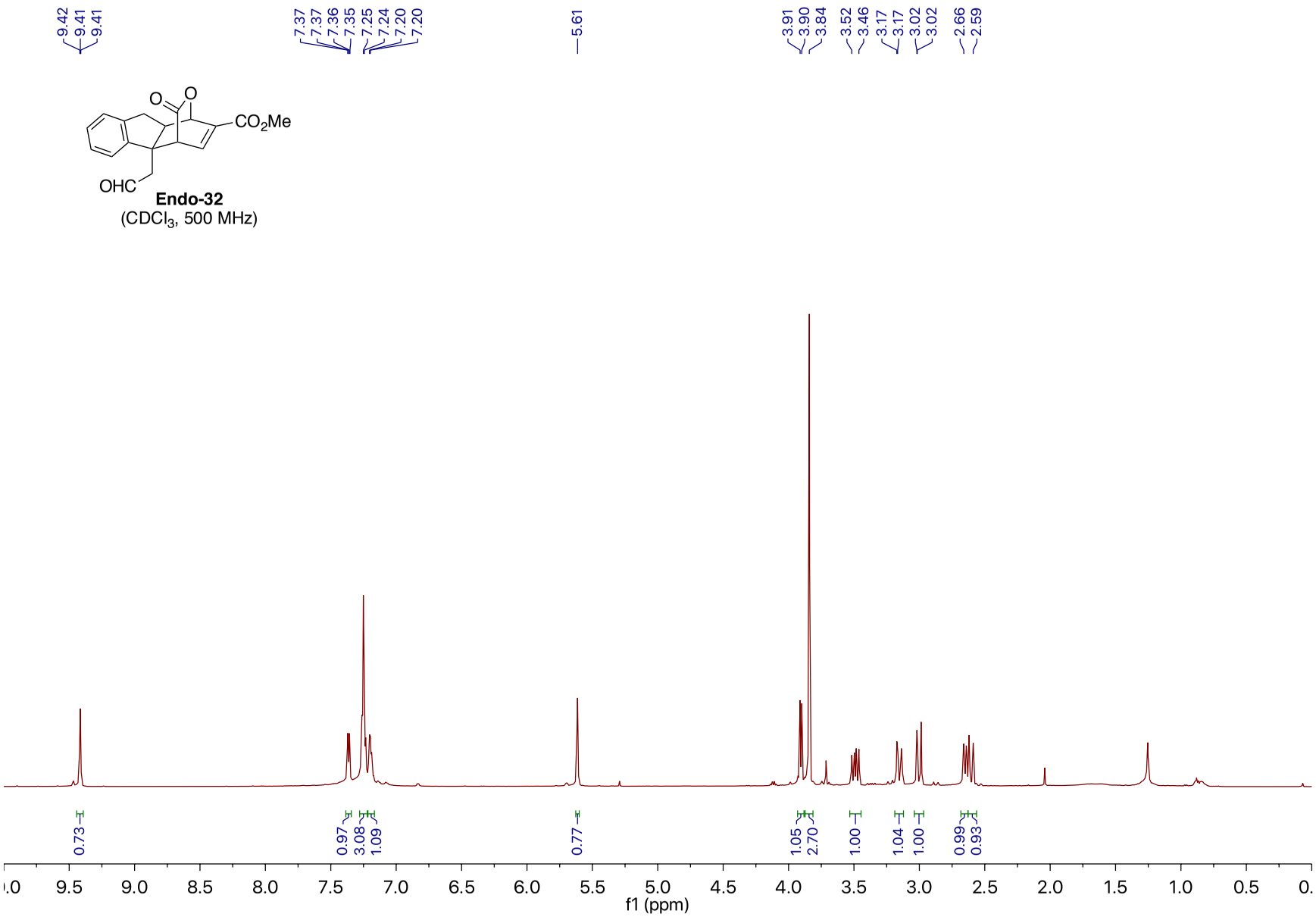

199.11
171.87
163.14
140.25
135.82
79.11
77.16
53.92
52.43
52.27
49.28
43.23
33.16
29.12
26.30
25.97
25.76
25.34
O
O
CHO
MeO2C
Exo-30
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

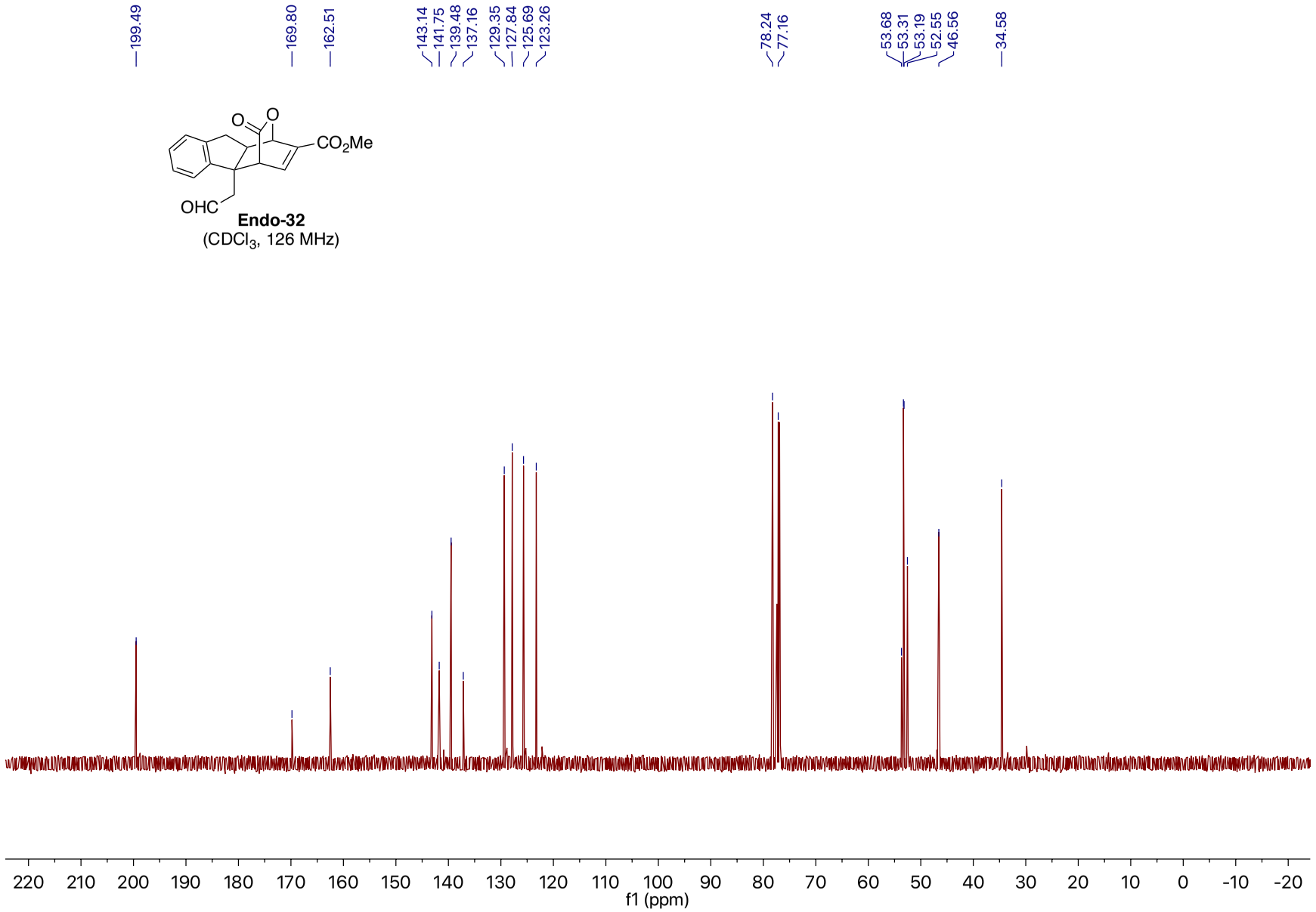


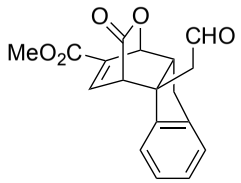
Endo-31
($CDCl_3$, 500 MHz)



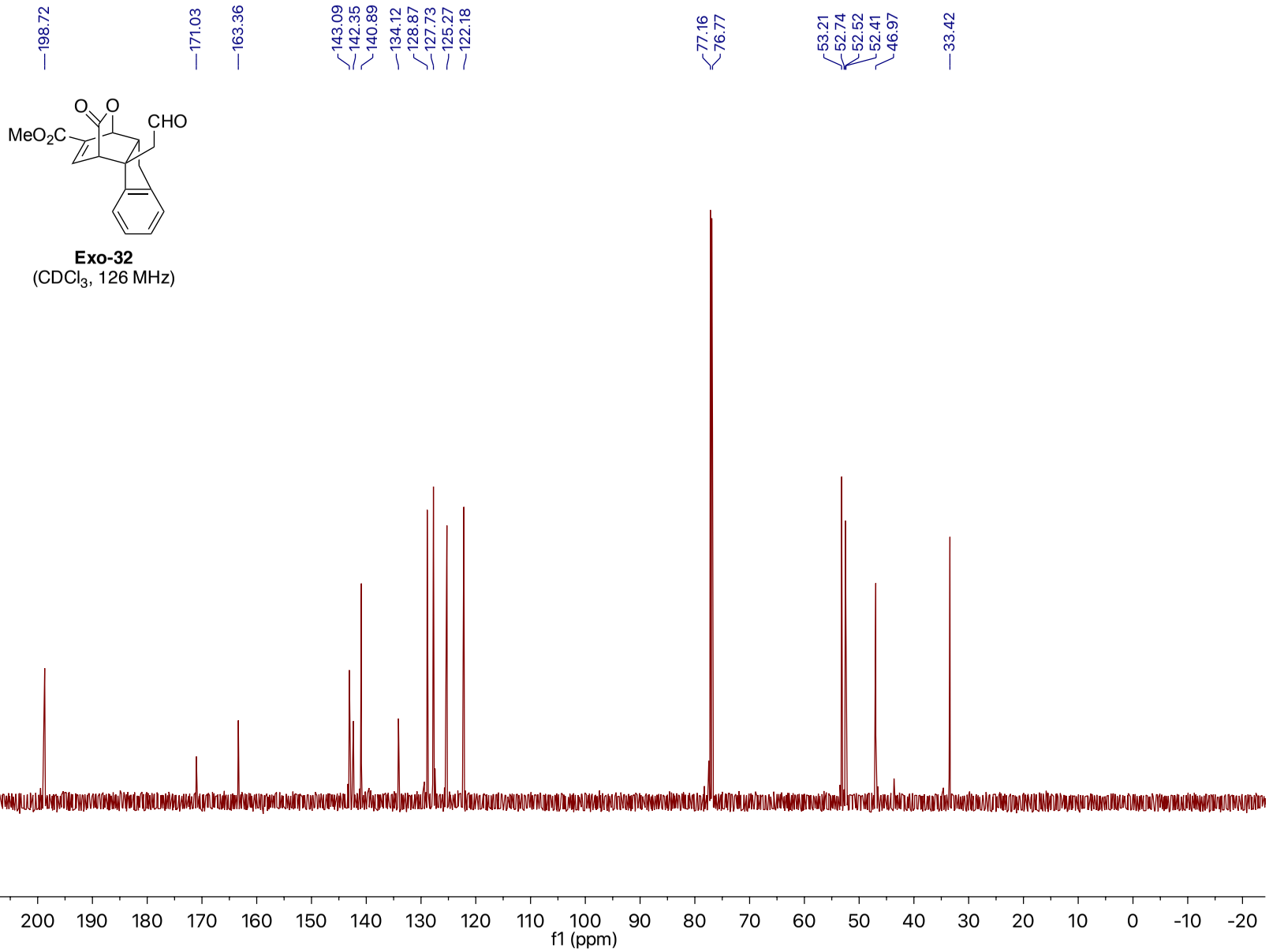
Endo-31
($CDCl_3$, 126 MHz)


9.42
9.41
9.41
7.37
7.37
7.36
7.35
7.25
7.24
7.20
7.20
5.61
3.91
3.90
3.84
3.52
3.46
3.17
3.17
3.02
3.02
2.66
2.59
O
O
CO2Me
OHC
Endo-32
(CDCl3, 500 MHz)
0.73
0.97
3.08
1.09
0.77
1.05
2.70
1.00
1.04
1.00
0.99
0.93
f1 (ppm)

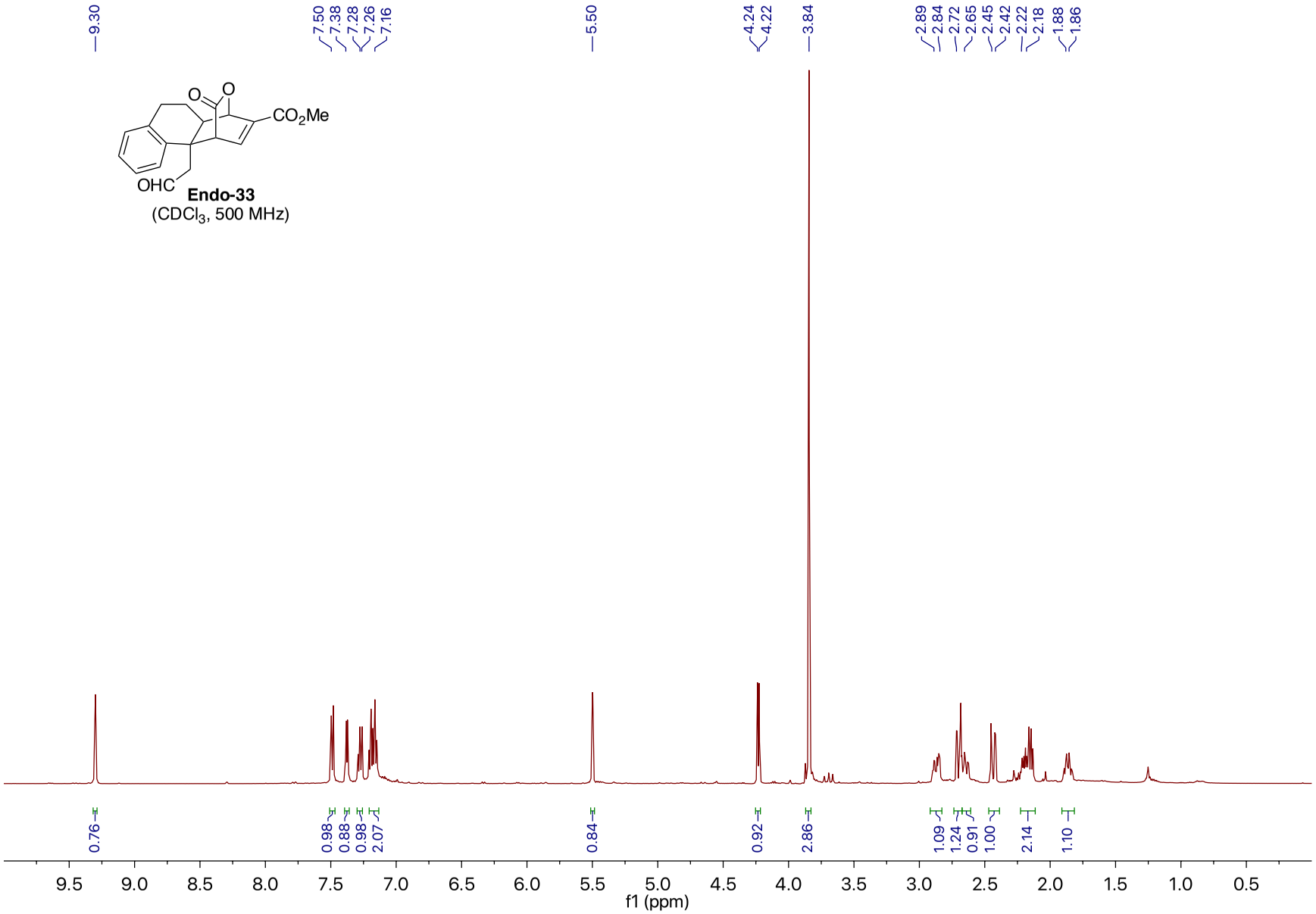

199.49
169.80
162.51
143.14
141.75
139.48
137.16
129.35
127.84
125.69
123.26
78.24
77.16
53.68
53.31
53.19
52.55
46.56
34.58
O
O
CO2Me
OHC
Endo-32
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

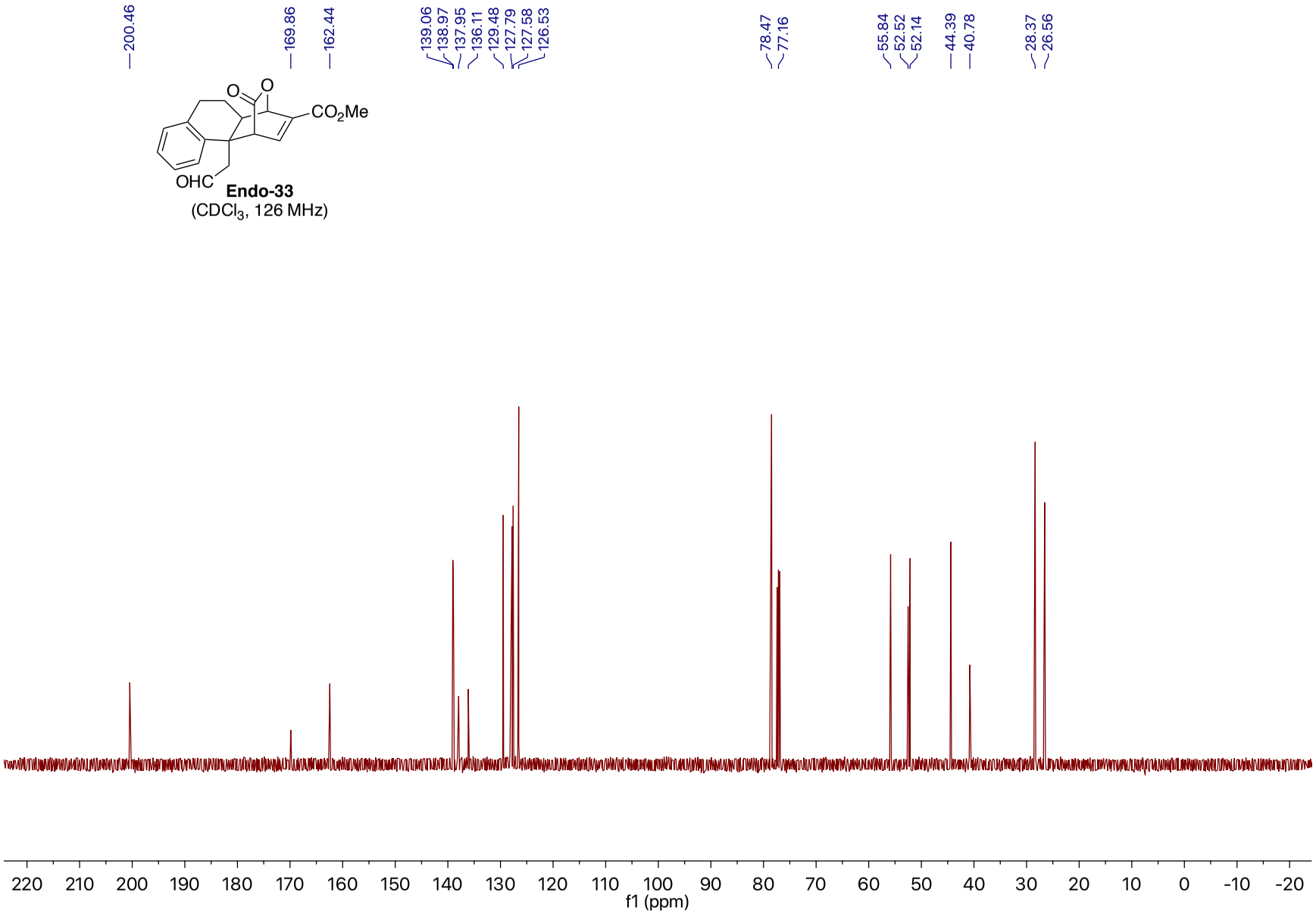


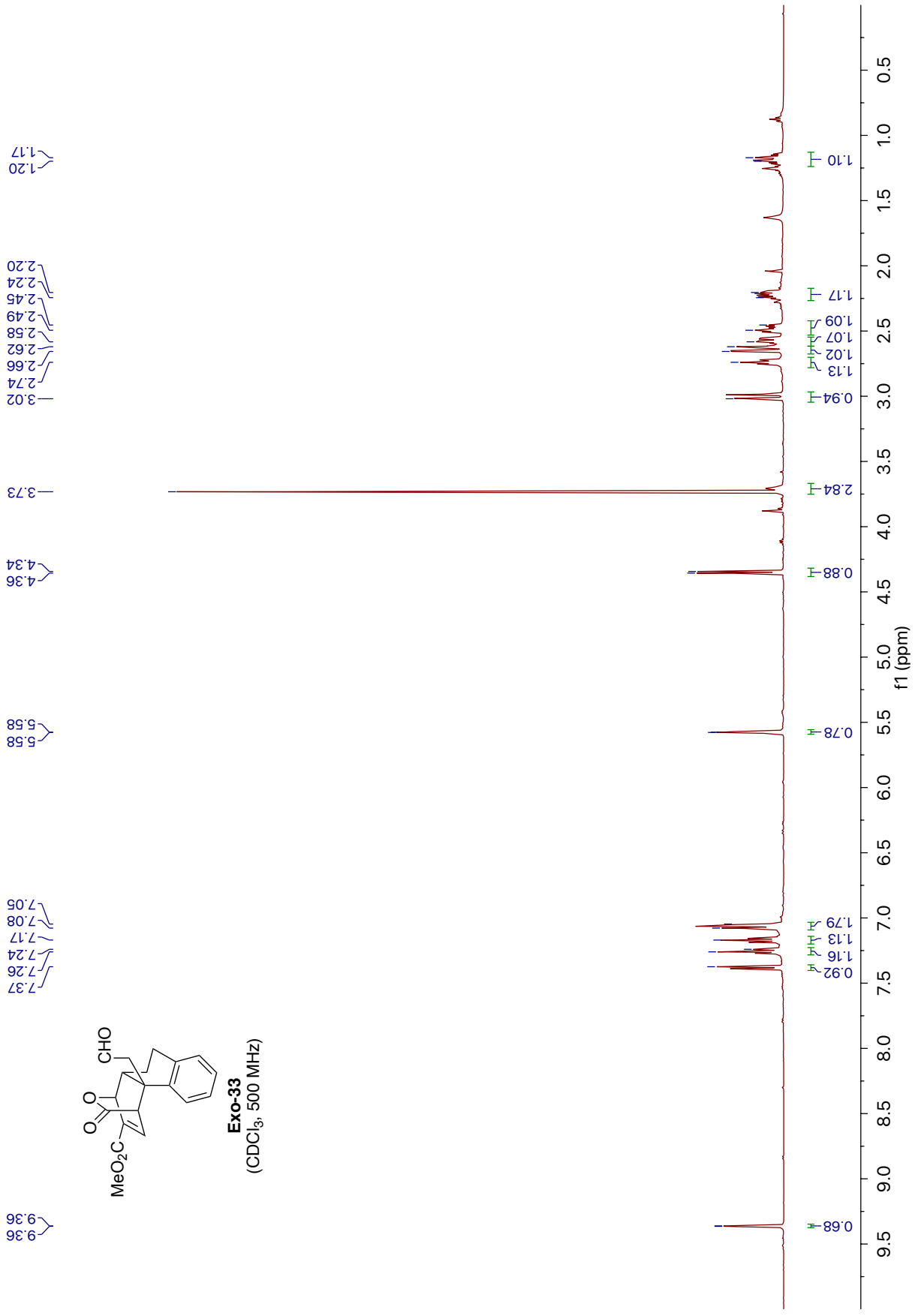
Exo-32
($CDCl_3$, 500 MHz)

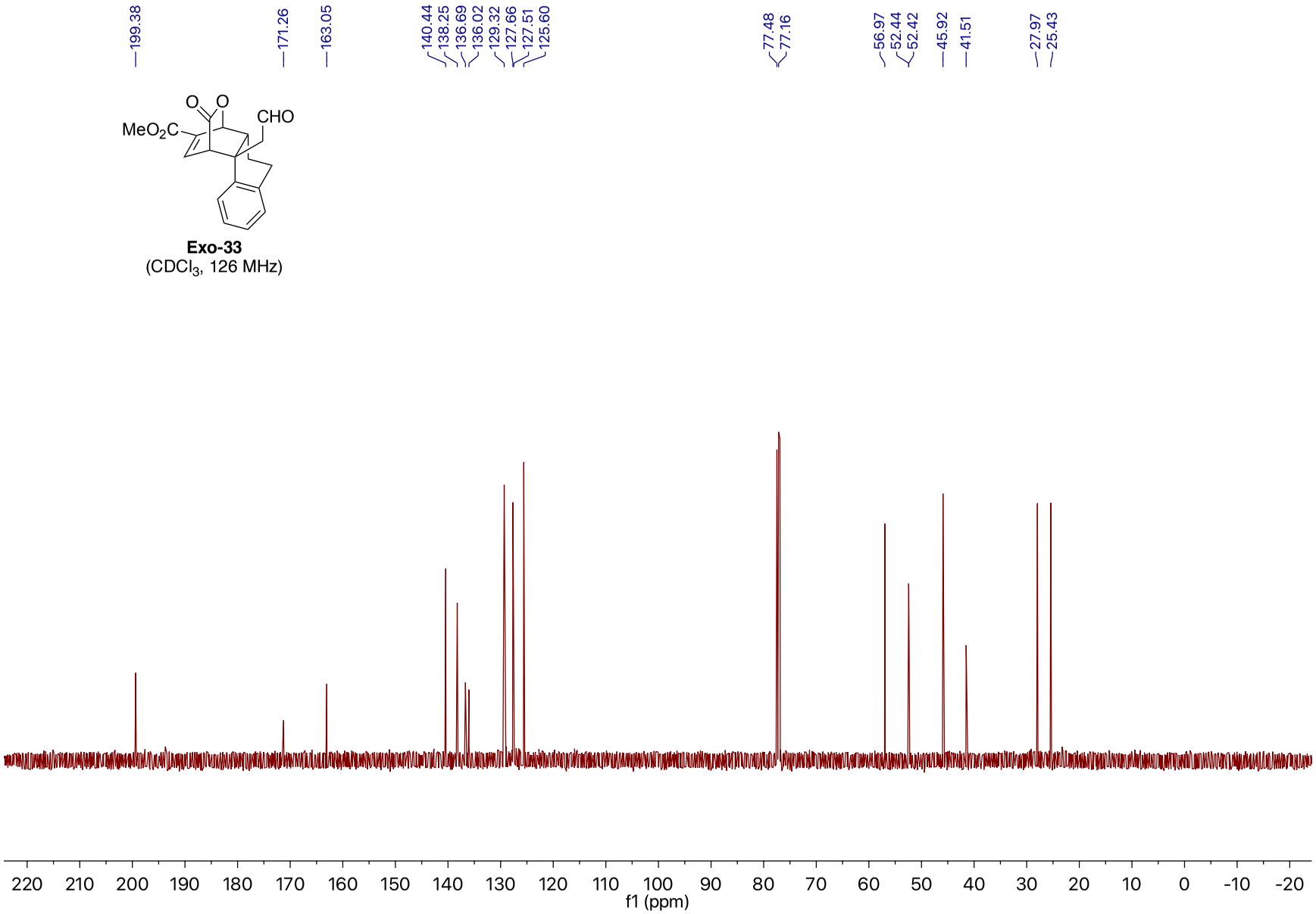


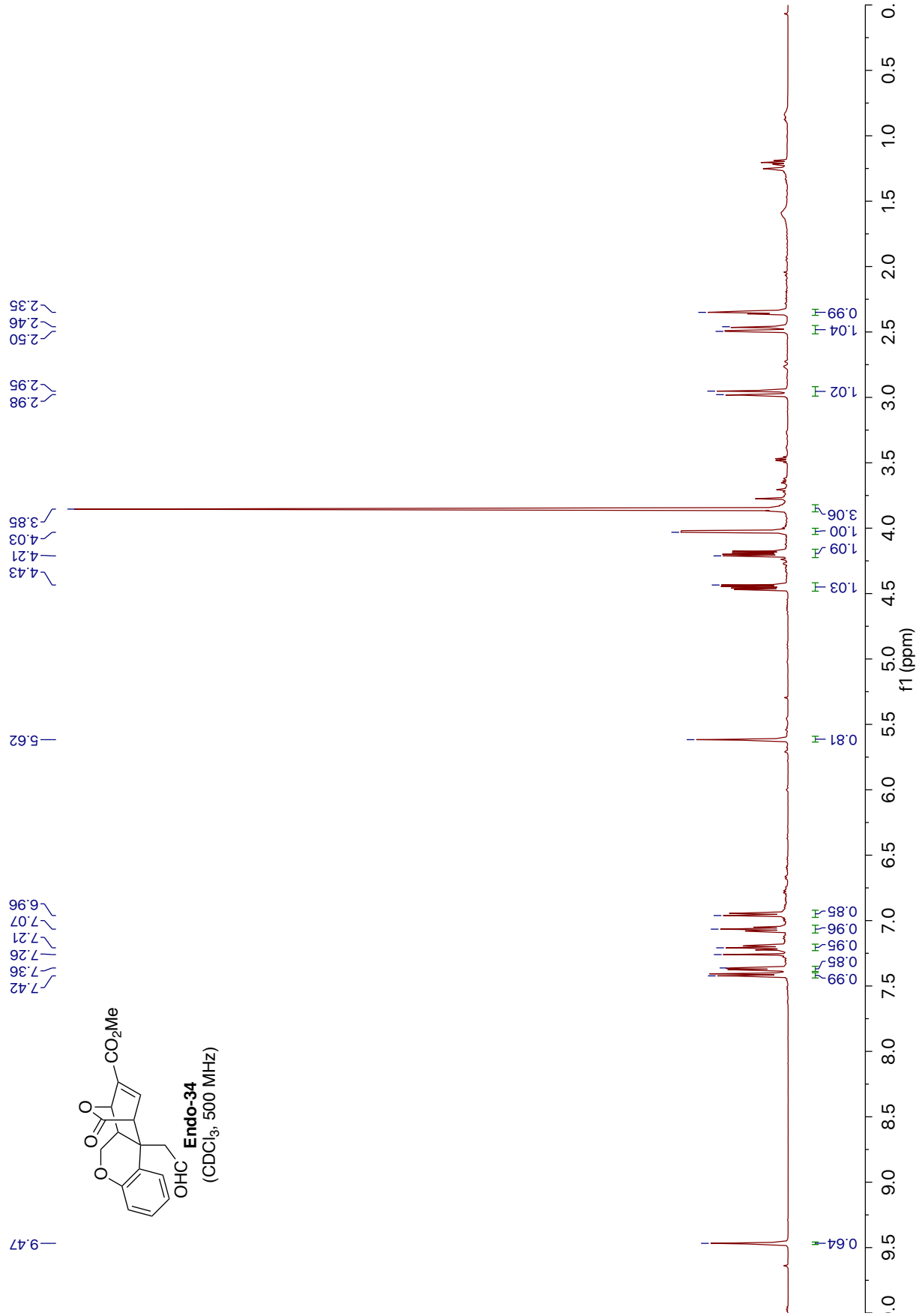
Exo-32
($CDCl_3$, 126 MHz)

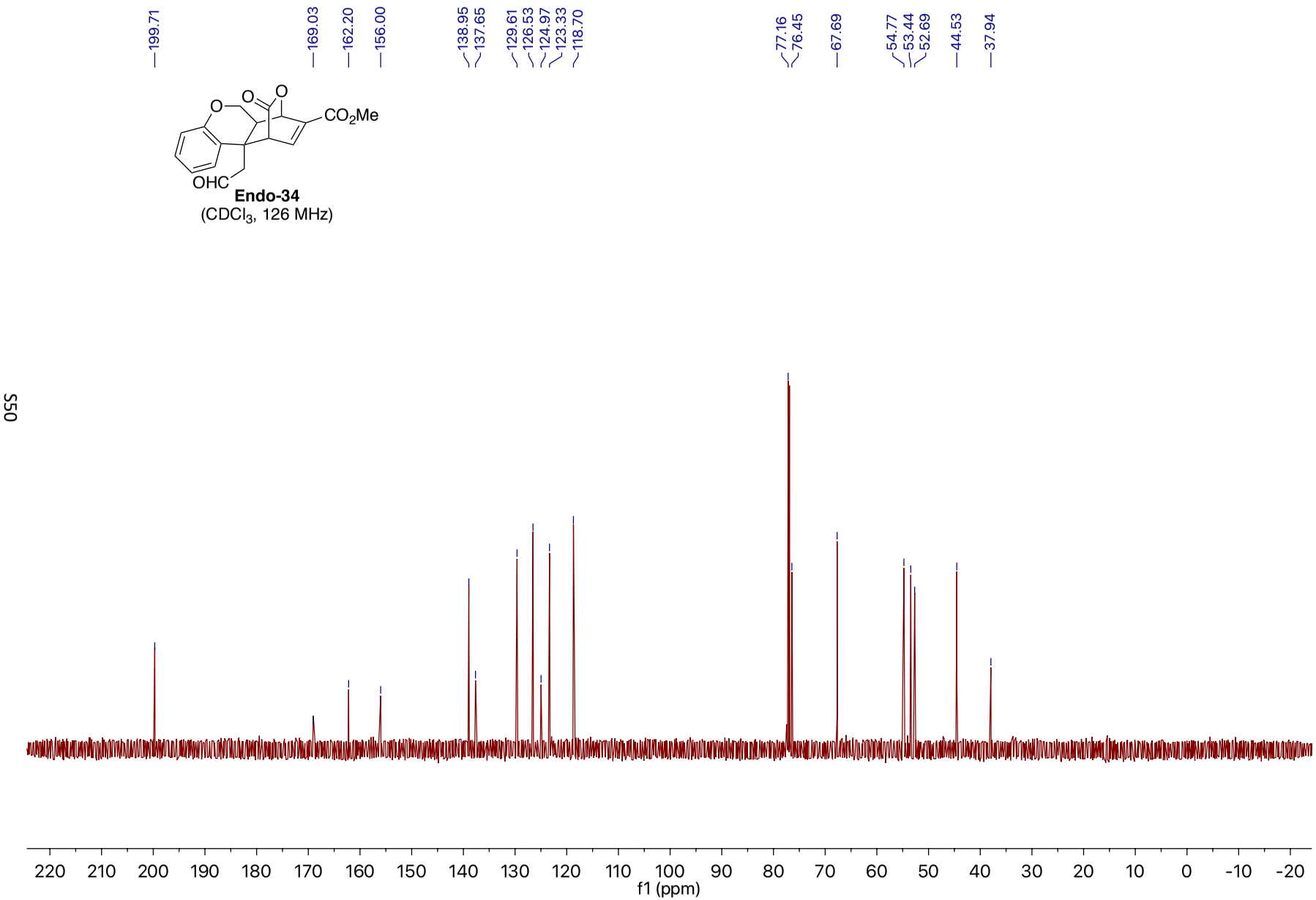

9.30
7.50
7.38
7.28
7.26
7.16
5.50
4.24
4.22
3.84
2.89
2.84
2.72
2.65
2.45
2.42
2.22
2.18
1.88
1.86
O
O
CO2Me
OHC
Endo-33
(CDCl3, 500 MHz)
0.76
0.98
0.88
0.98
2.07
0.84
0.92
2.86
1.09
1.24
0.91
1.00
2.14
1.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

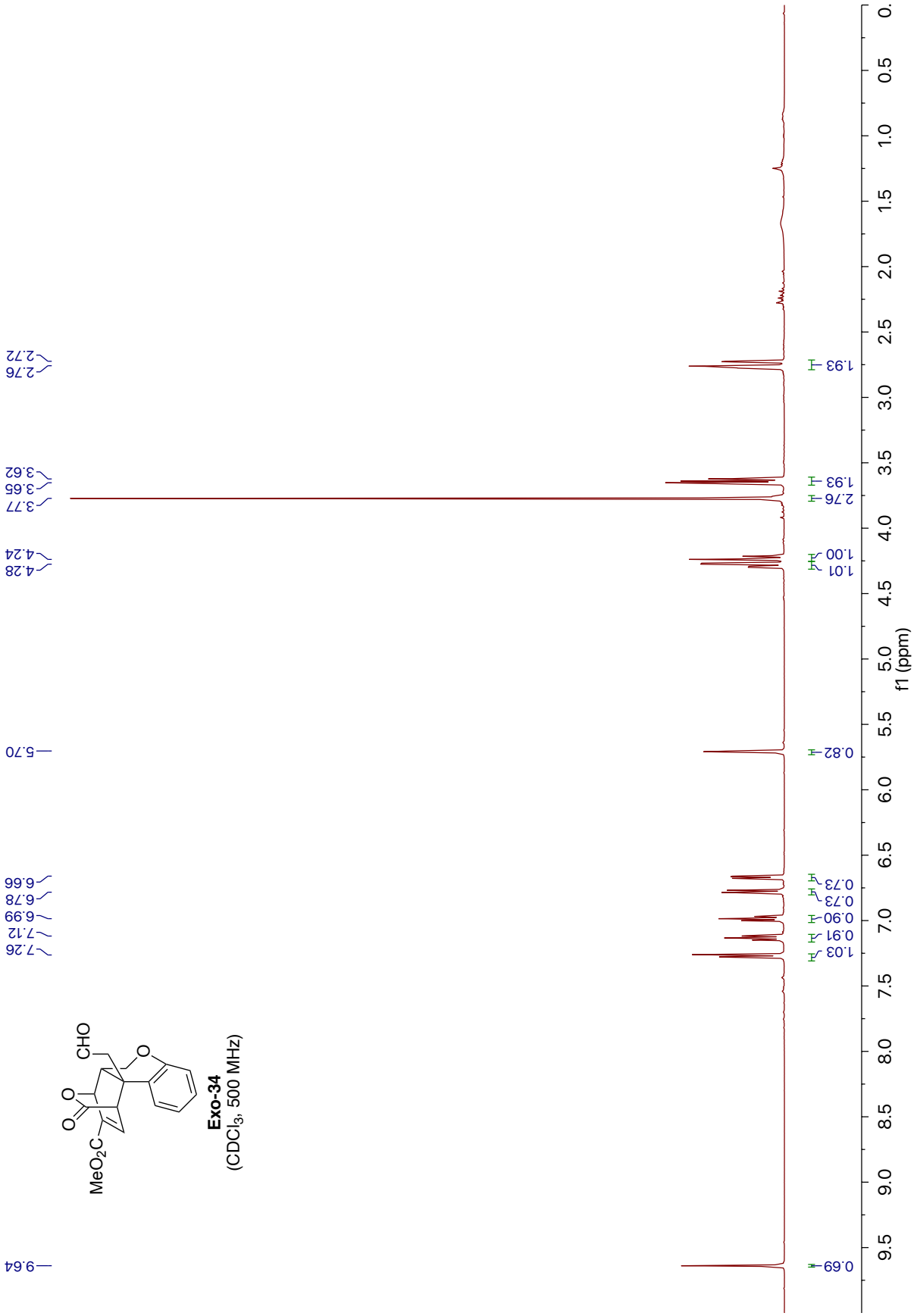

200.46
169.86
162.44
139.06
138.97
137.95
136.11
129.48
127.79
127.58
126.53
78.47
77.16
55.84
52.52
52.14
44.39
40.78
28.37
26.56
O
O
CO2Me
OHC
Endo-33
(CDCl3, 126 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

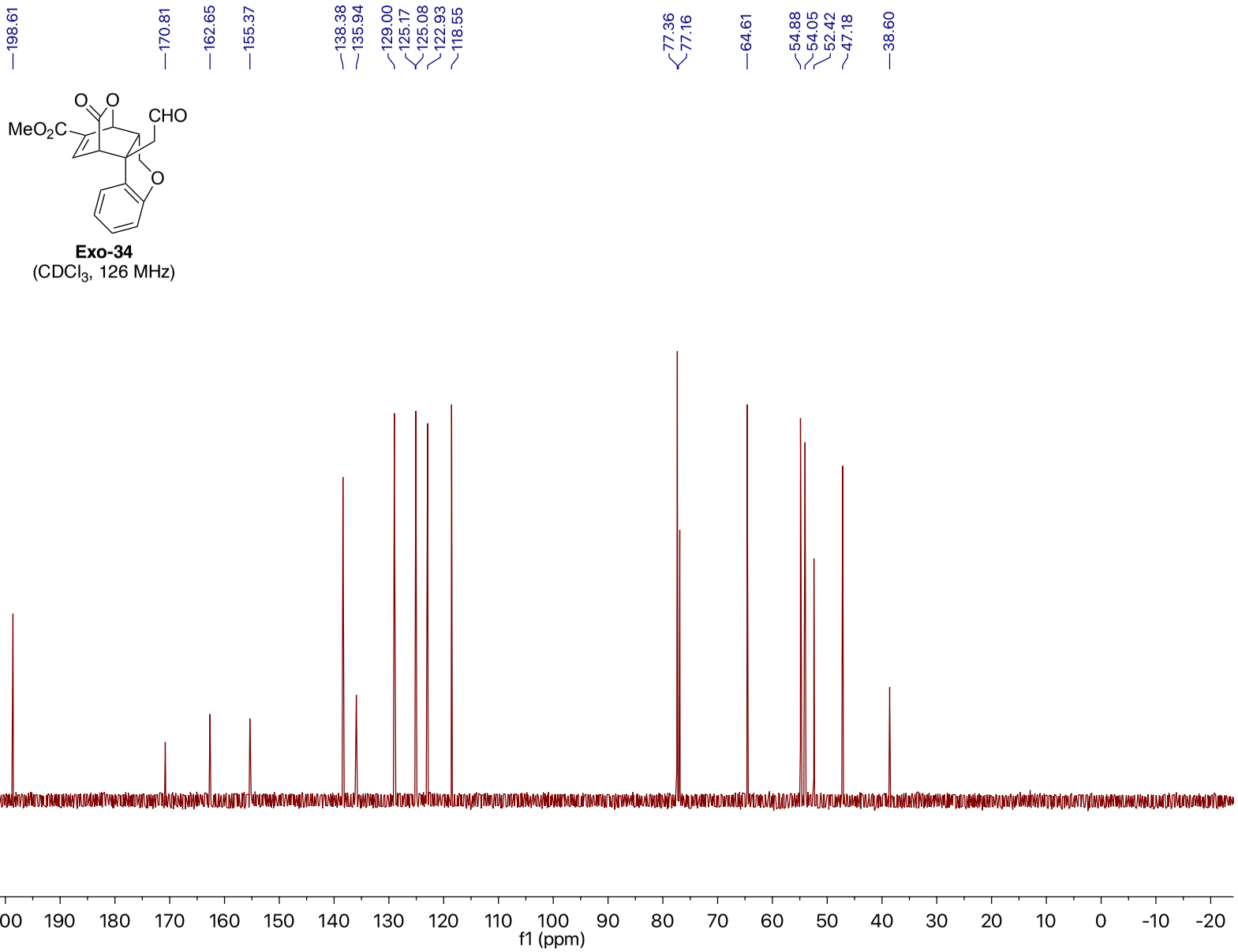

CHO
O
O
MeO2C
Exo-33
(CDCl3, 500 MHz)
9.36
7.37
7.26
7.24
7.17
7.08
7.05
5.58
4.36
4.34
3.73
3.02
2.74
2.66
2.62
2.58
2.49
2.45
2.24
2.20
1.20
1.17
0.68
0.92
1.16
1.13
1.79
0.78
0.88
2.84
0.94
1.13
1.02
1.07
1.09
1.17
1.10
f1 (ppm)

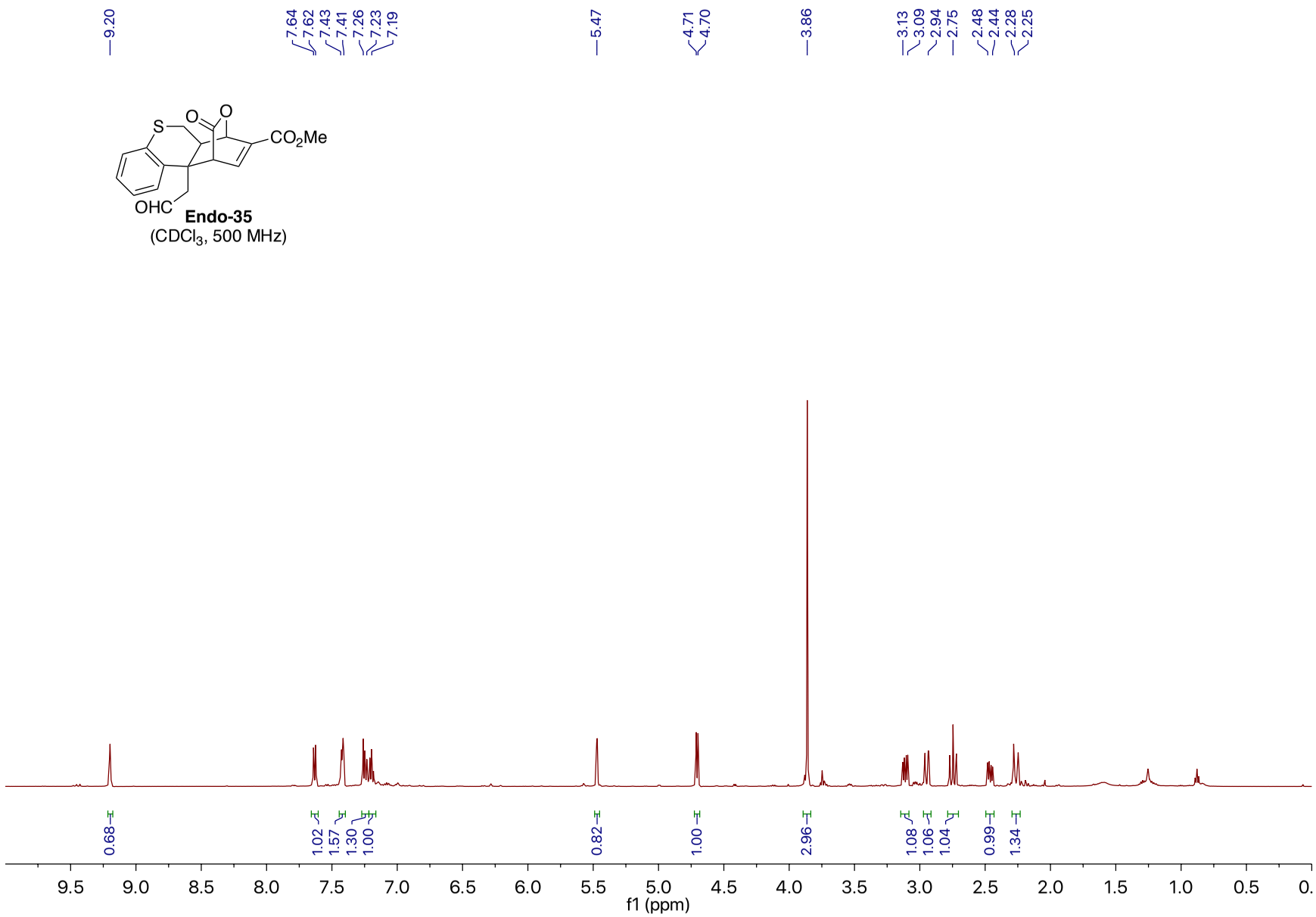

199.38
171.26
163.05
140.44
138.25
136.69
136.02
129.32
127.66
127.51
125.60
77.48
77.16
56.97
52.44
52.42
45.92
41.51
27.97
25.43
O
O
MeO2C
CHO
Exo-33
(CDCl3, 126 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

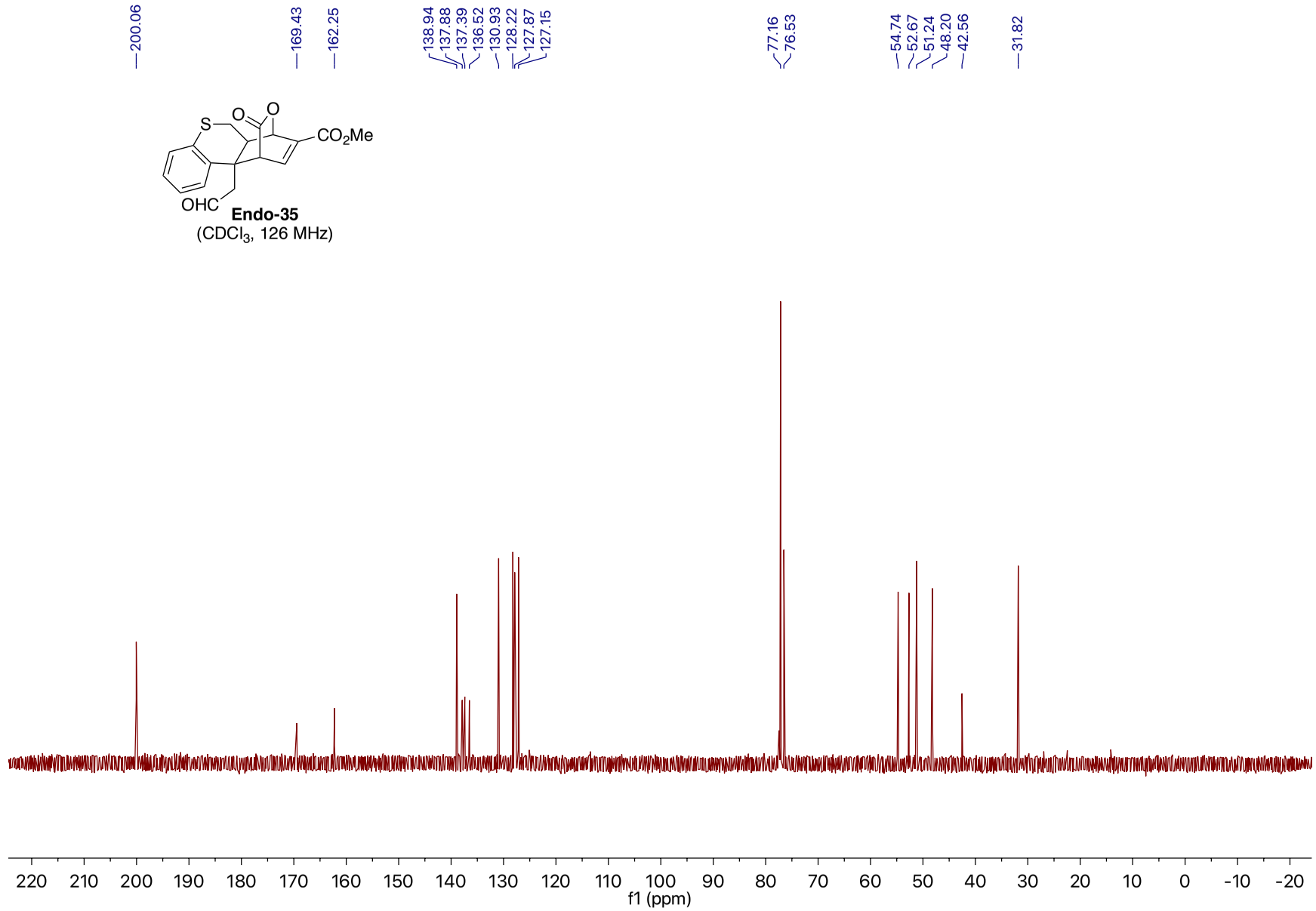

Endo-34
(CDCl3, 500 MHz)
CO2Me
OHC
O
O
O
9.47
7.42
7.36
7.26
7.21
7.07
6.96
5.62
4.43
4.21
4.03
3.85
2.98
2.95
2.50
2.46
2.35
0.64
0.99
0.85
0.85
0.96
0.95
0.85
1.02
1.03
1.09
1.00
3.06
0.81
0.99
1.04
f1 (ppm)


199.71
169.03
162.20
156.00
138.95
137.65
129.61
126.53
124.97
123.33
118.70
77.16
76.45
67.69
54.77
53.44
52.69
44.53
37.94
O
O
O
O
CO2Me
OHC
Endo-34
(CDCl3, 126 MHz)
550
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

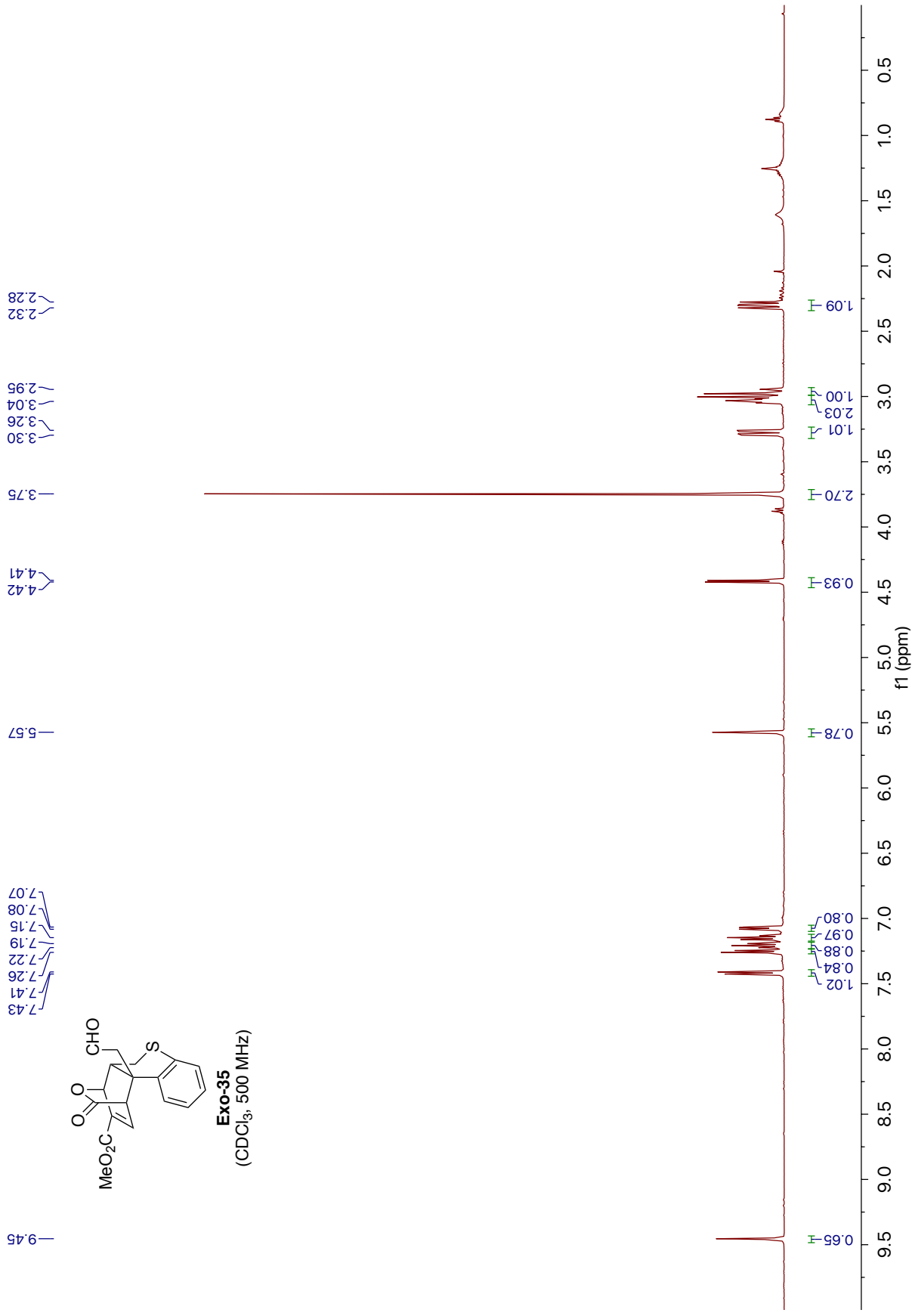

CHO
O
O
O
MeO2C
Exo-34
(CDCl3, 500 MHz)
9.64
7.26
7.12
6.99
6.78
6.66
5.70
4.28
4.24
3.77
3.65
3.62
2.76
2.72
0.69
1.03
0.91
0.90
0.73
0.73
0.82
1.01
1.00
2.76
1.93
1.93
f1 (ppm)

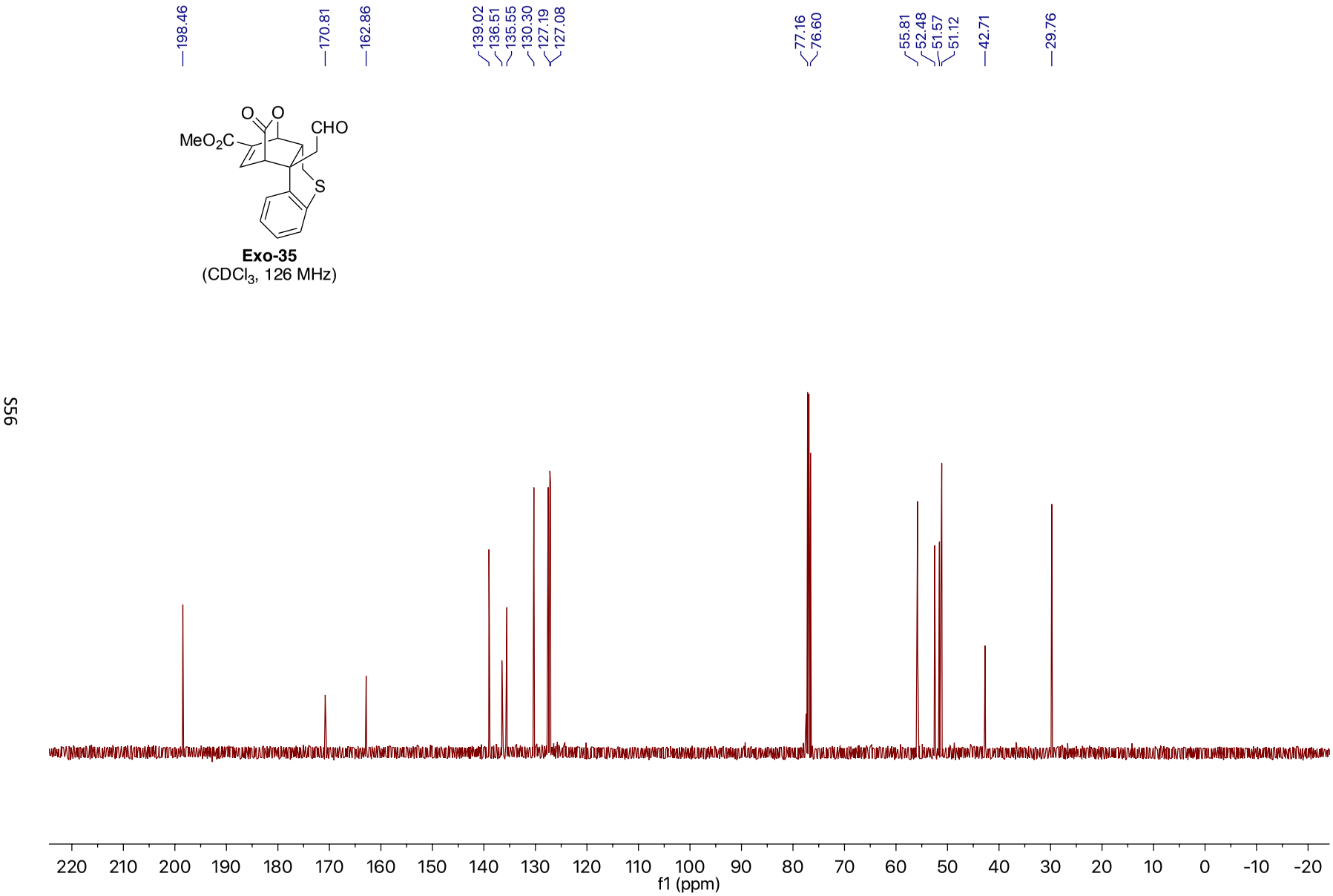

198.61
170.81
162.65
155.37
138.38
135.94
129.00
125.17
125.08
122.93
118.55
77.36
77.16
64.61
54.88
54.05
52.42
47.18
38.60
O
O
CHO
MeO2C
O
Exo-34
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

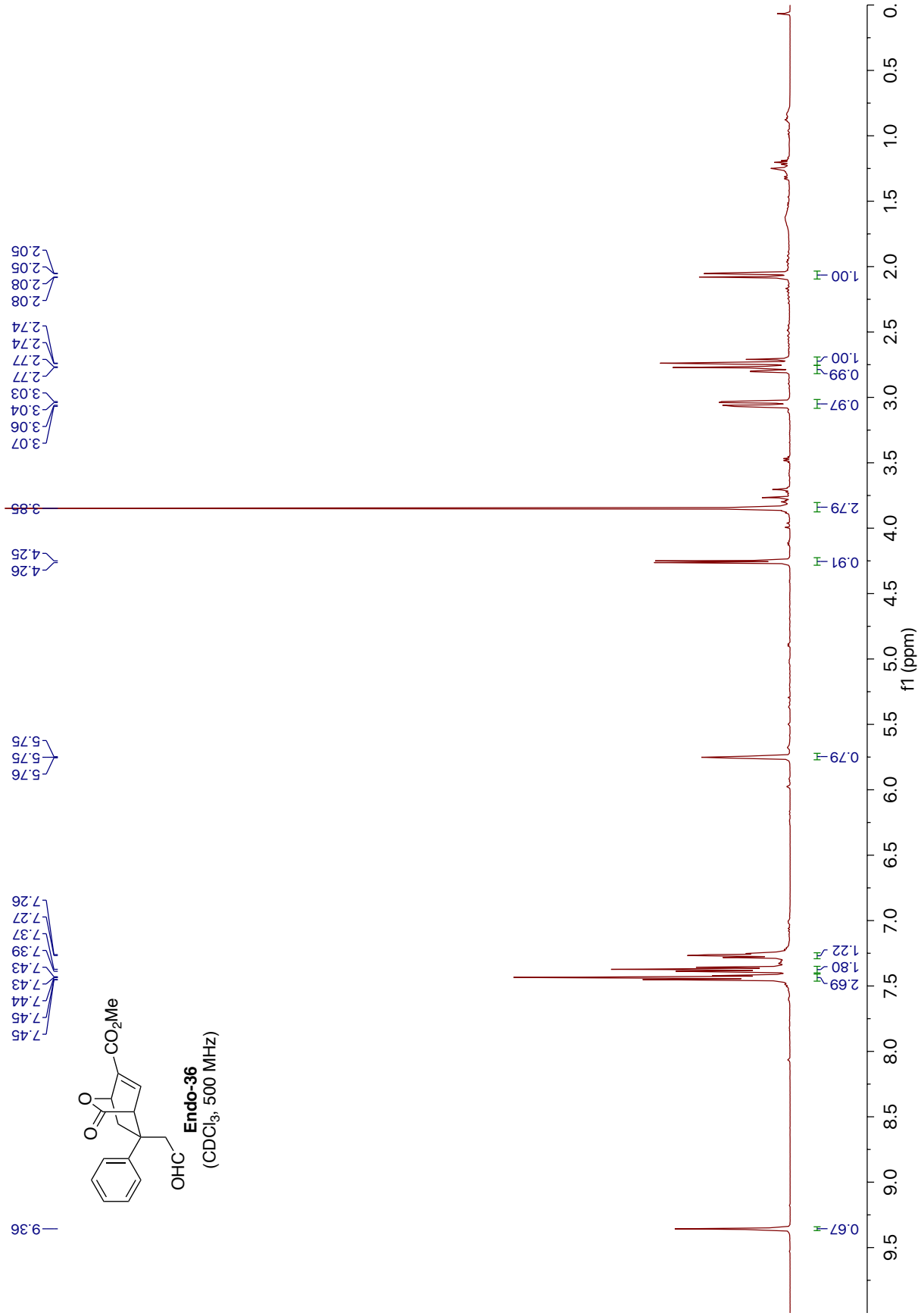

9.20
7.64
7.62
7.43
7.41
7.26
7.23
7.19
5.47
4.71
4.70
3.86
3.13
3.09
2.94
2.75
2.48
2.44
2.28
2.25
O
O
S
CO2Me
OHC
Endo-35
(CDCl3, 500 MHz)
0.68
1.02
1.57
1.30
1.00
0.82
1.00
2.96
1.08
1.06
1.04
0.99
1.34
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

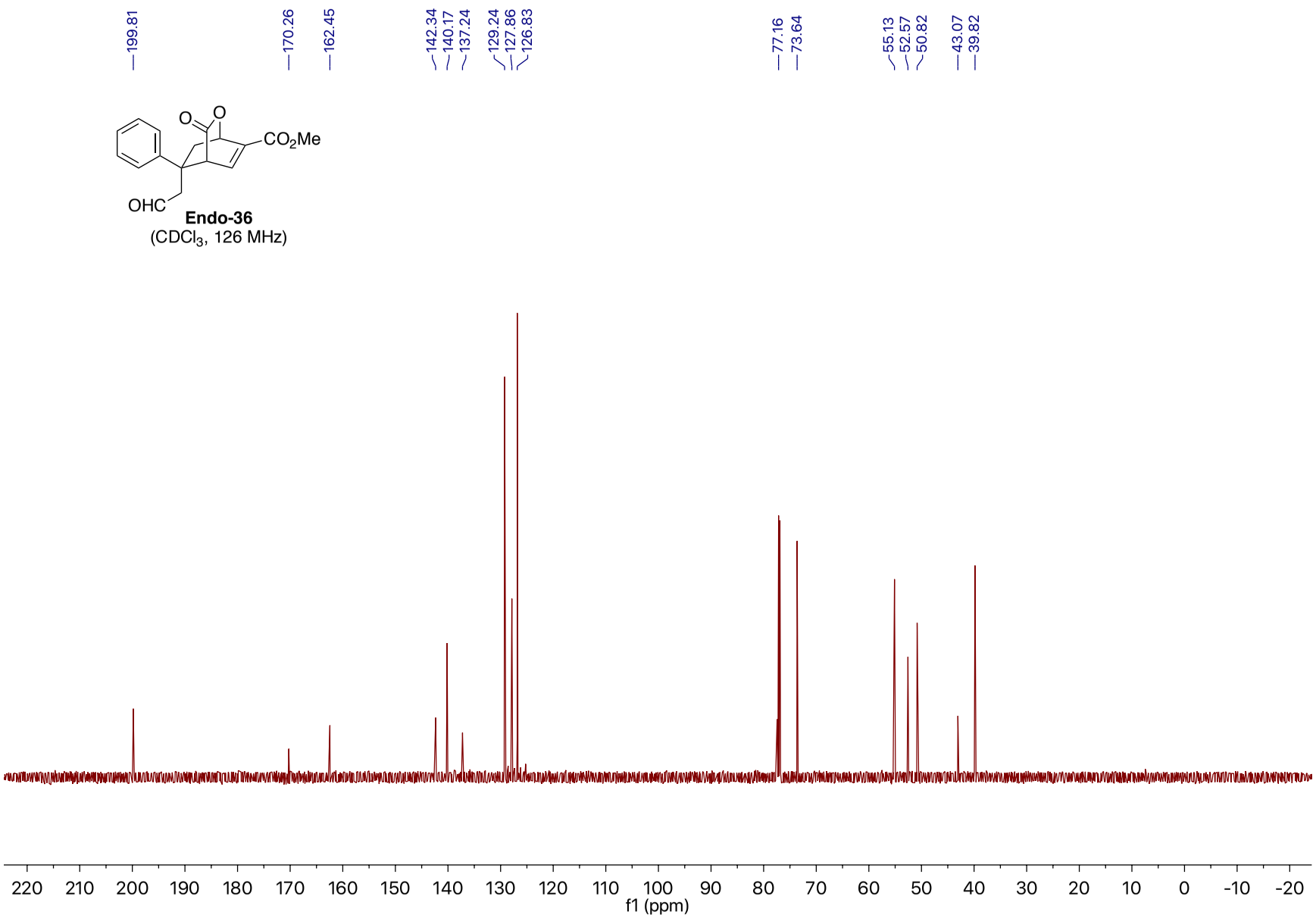


Endo-35
($CDCl_3$, 126 MHz)

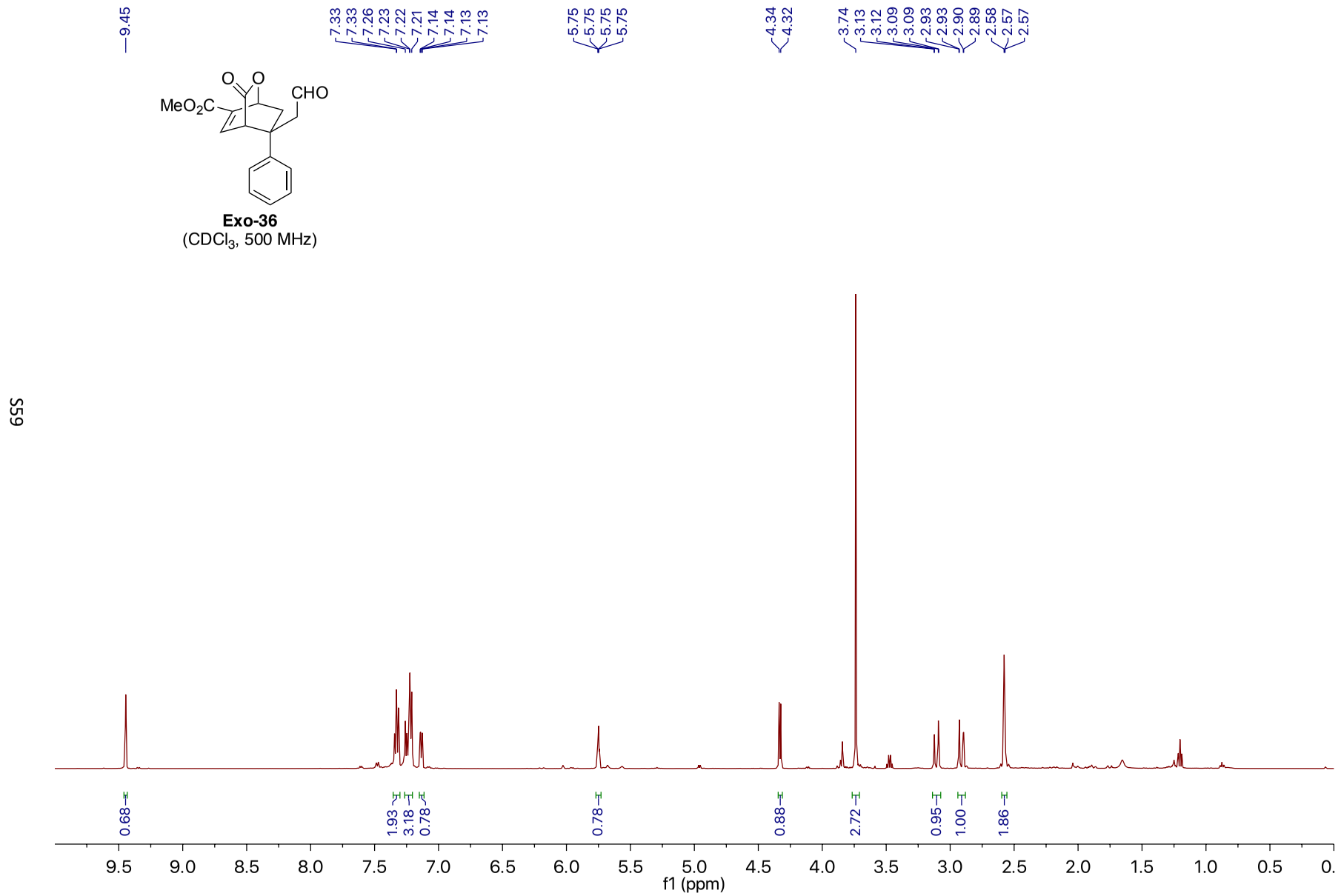

CHO
S
O
O
MeO2C
Exo-35
(CDCl3, 500 MHz)
9.45
7.43
7.41
7.26
7.22
7.19
7.15
7.08
7.07
5.57
4.42
4.41
3.75
3.30
3.26
3.04
2.95
2.32
2.28
0.65
1.09
1.00
2.03
1.01
2.70
0.93
0.78
1.02
0.84
0.88
0.97
0.80
f1 (ppm)


198.46
170.81
162.86
139.02
136.51
135.55
130.30
127.19
127.08
77.16
76.60
55.81
52.48
51.57
51.12
42.71
29.76
O
O
CHO
MeO2C
S
Exo-35
(CDCl3, 126 MHz)
S56
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

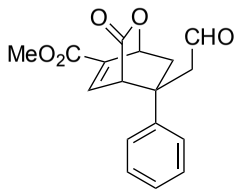

9.36
7.45
7.45
7.44
7.43
7.43
7.43
7.39
7.37
7.27
7.26
5.76
5.75
5.75
4.26
4.25
3.85
3.07
3.06
3.04
3.03
2.77
2.77
2.74
2.74
2.08
2.08
2.05
2.05
0.67
2.69
1.80
1.22
0.79
0.91
2.79
0.97
0.99
1.00
1.00
CO2Me
O
O
OHC
Endo-36
(CDCl3, 500 MHz)
f1 (ppm)



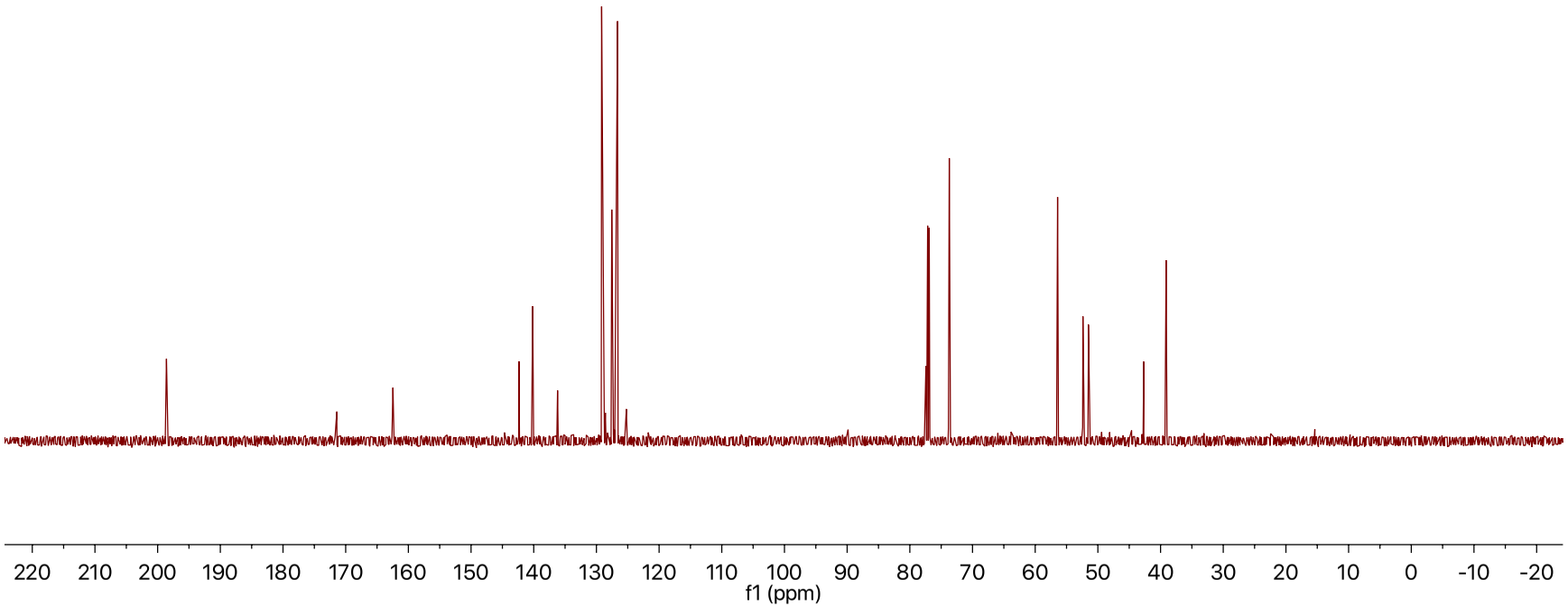
Endo-36
($CDCl_3$, 126 MHz)

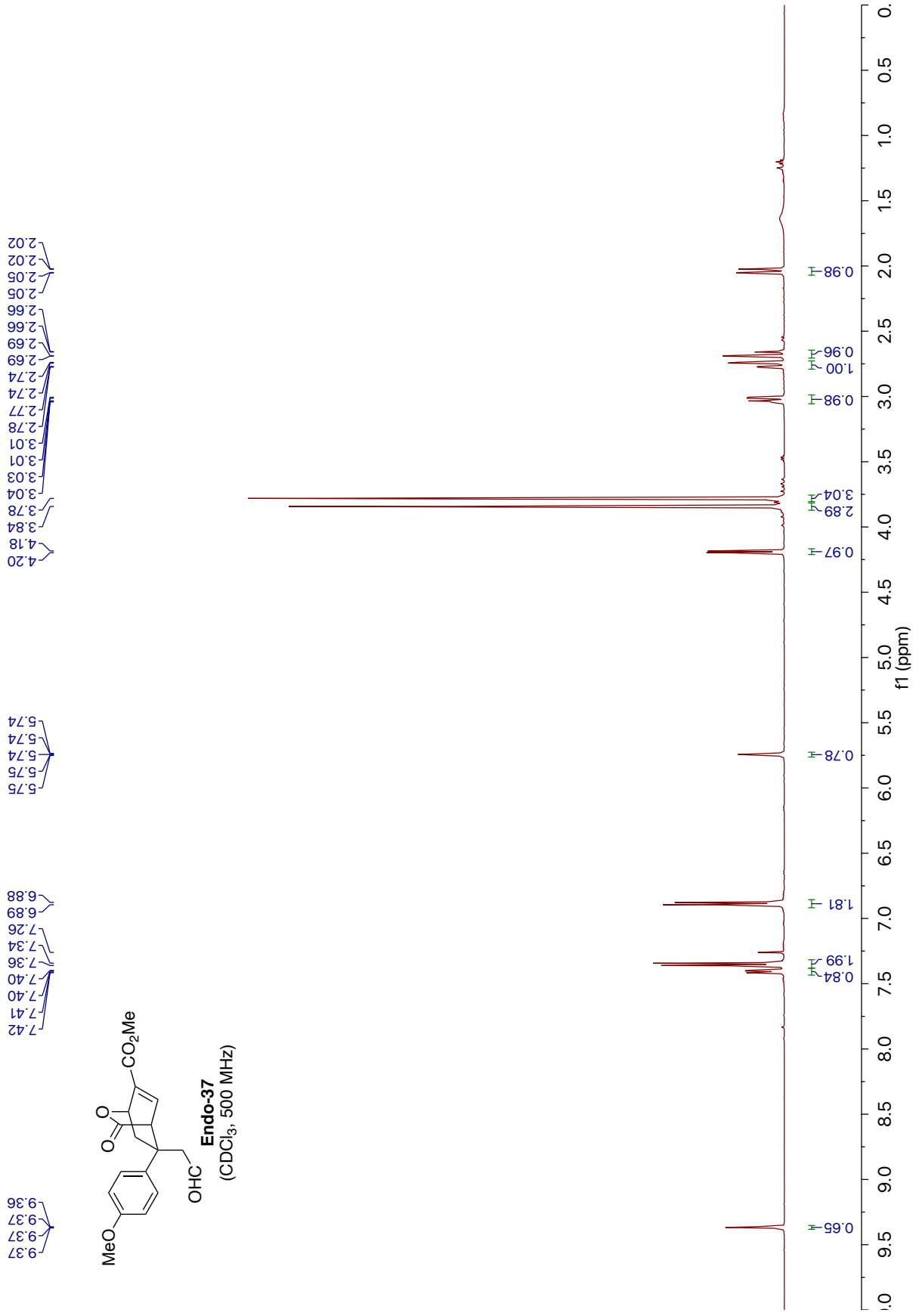

9.45
7.33
7.33
7.26
7.23
7.22
7.21
7.14
7.14
7.13
7.13
5.75
5.75
5.75
5.75
4.34
4.32
3.74
3.13
3.12
3.09
3.09
2.93
2.93
2.90
2.89
2.58
2.57
2.57
O
O
CHO
MeO2C
Exo-36
(CDCl3, 500 MHz)
0.68
1.93
3.18
0.78
0.78
0.88
2.72
0.95
1.00
1.86
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

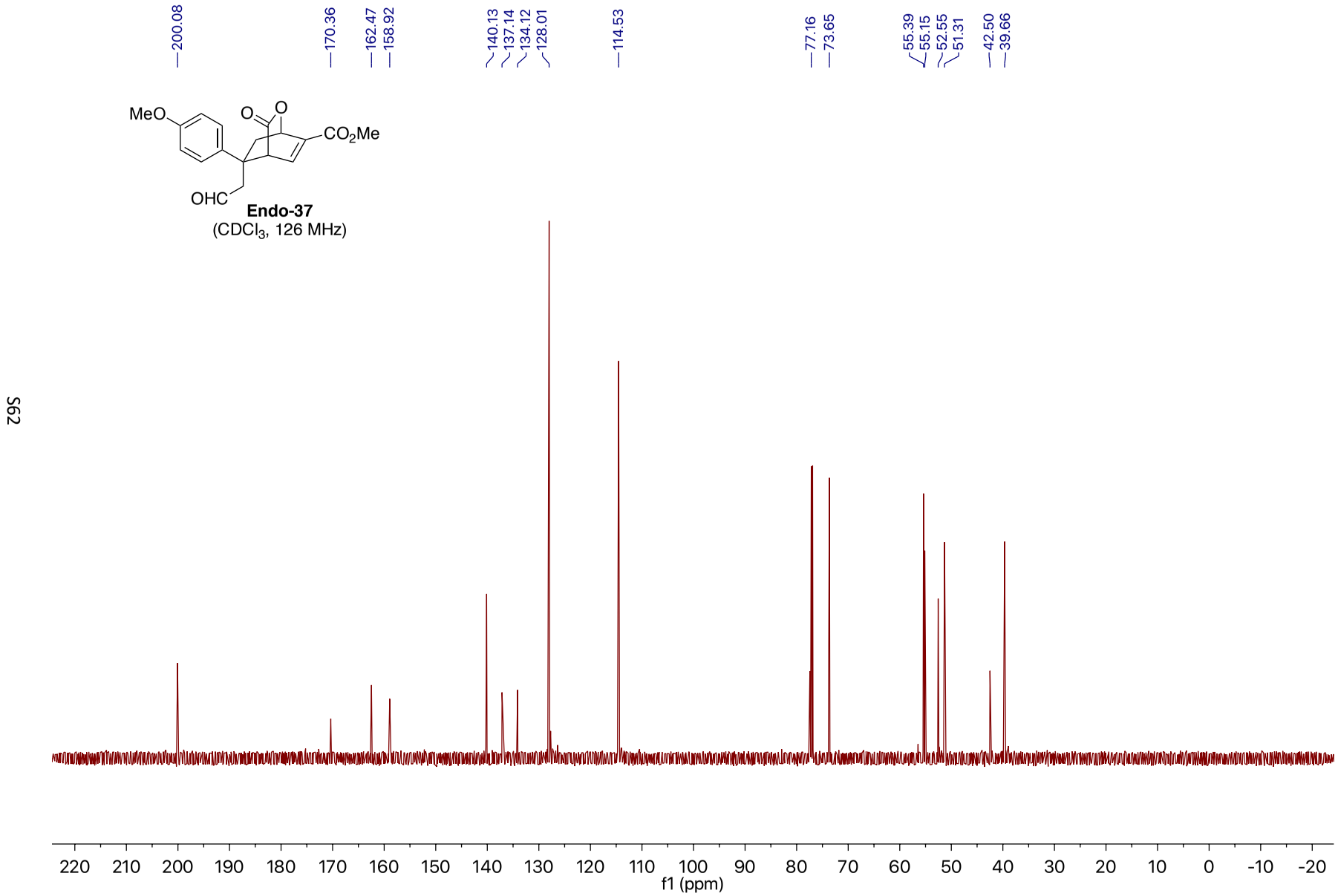
198.59
171.42
162.46
142.36
140.17
136.20
129.18
127.55
126.64
77.16
73.71
56.43
52.39
51.51
42.69
39.11

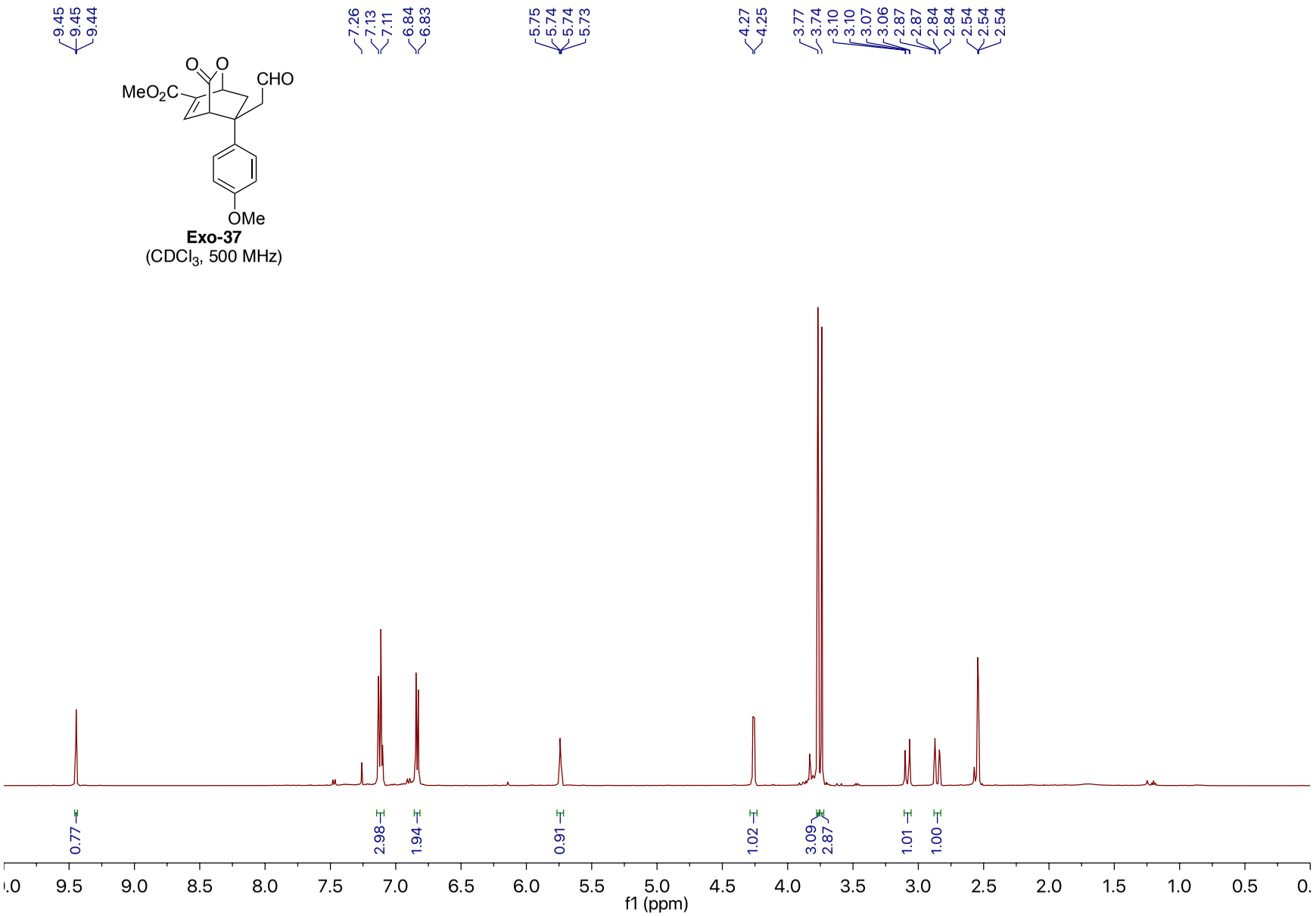


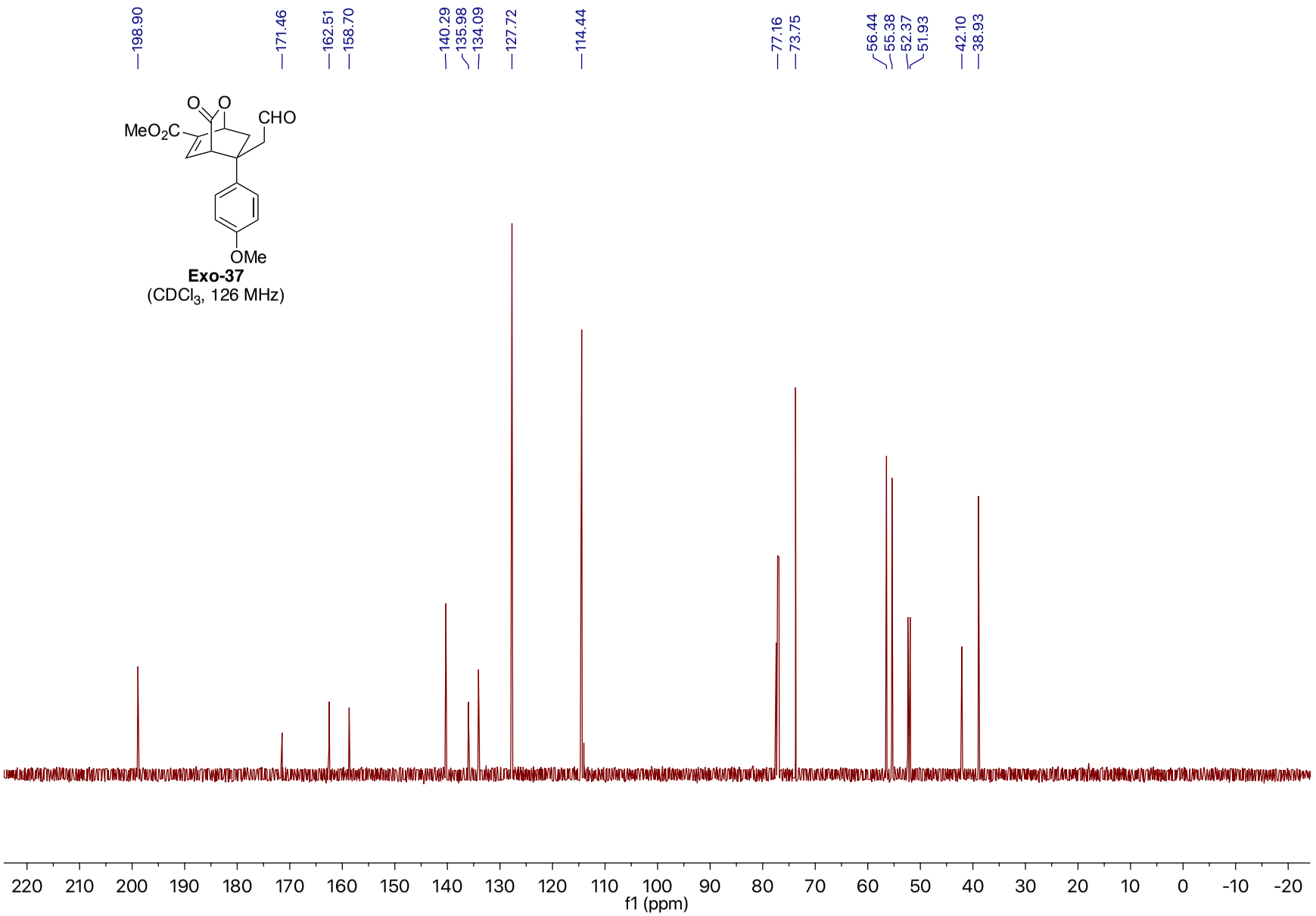
Exo-36
($CDCl_3$, 126 MHz)

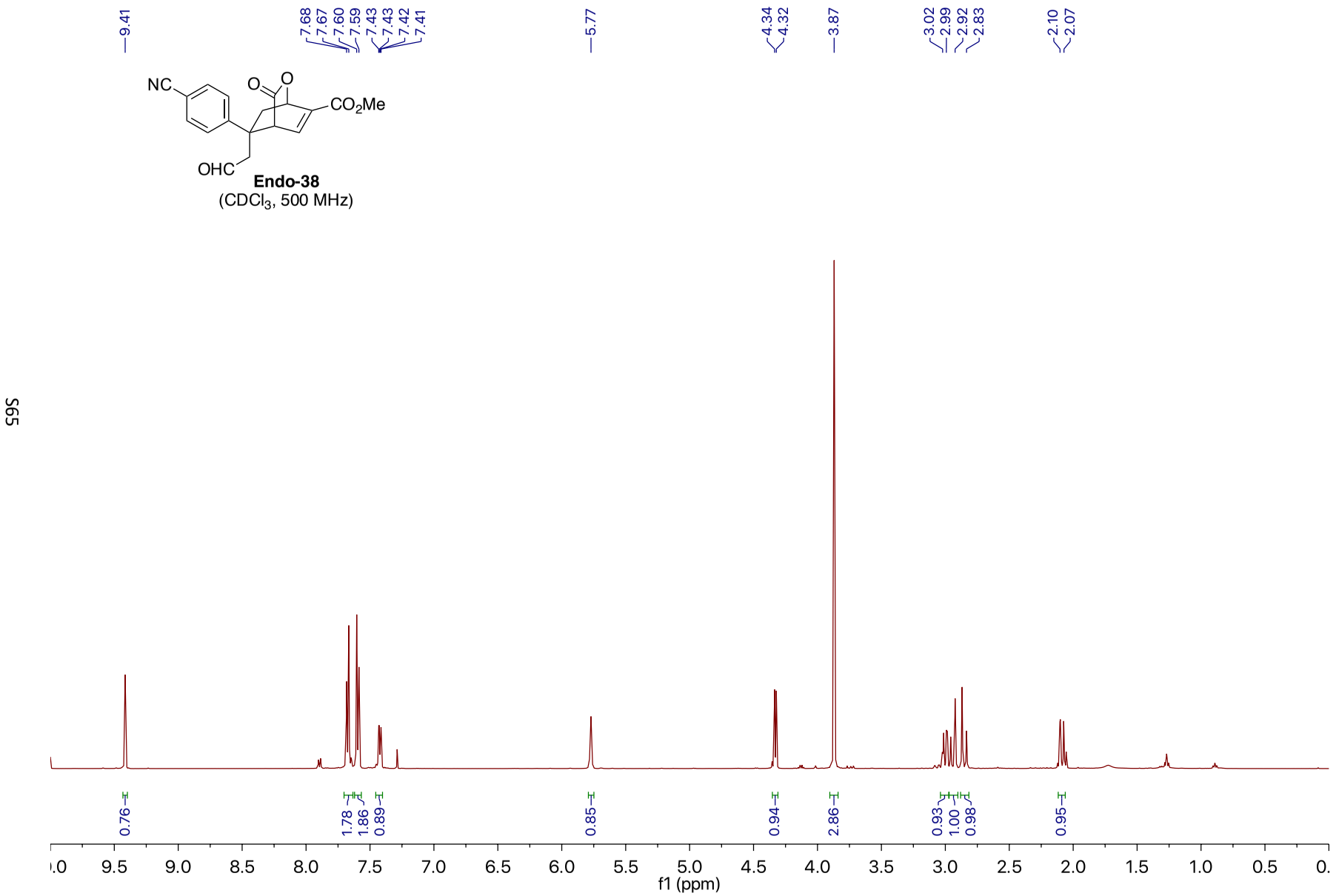


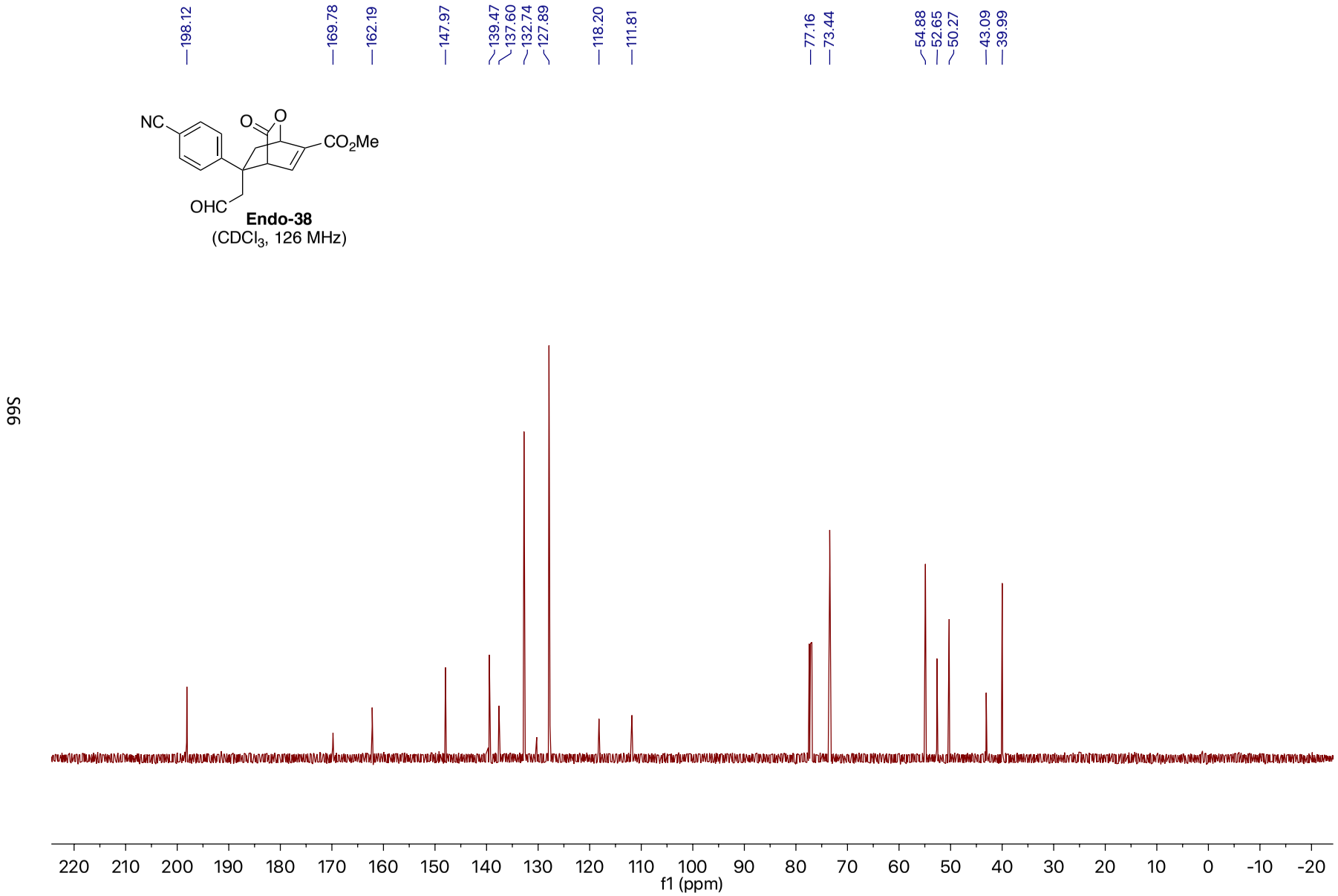

Endo-37
(CDCl3, 500 MHz)
CO2Me
O
O
OHC
MeO
f1 (ppm)

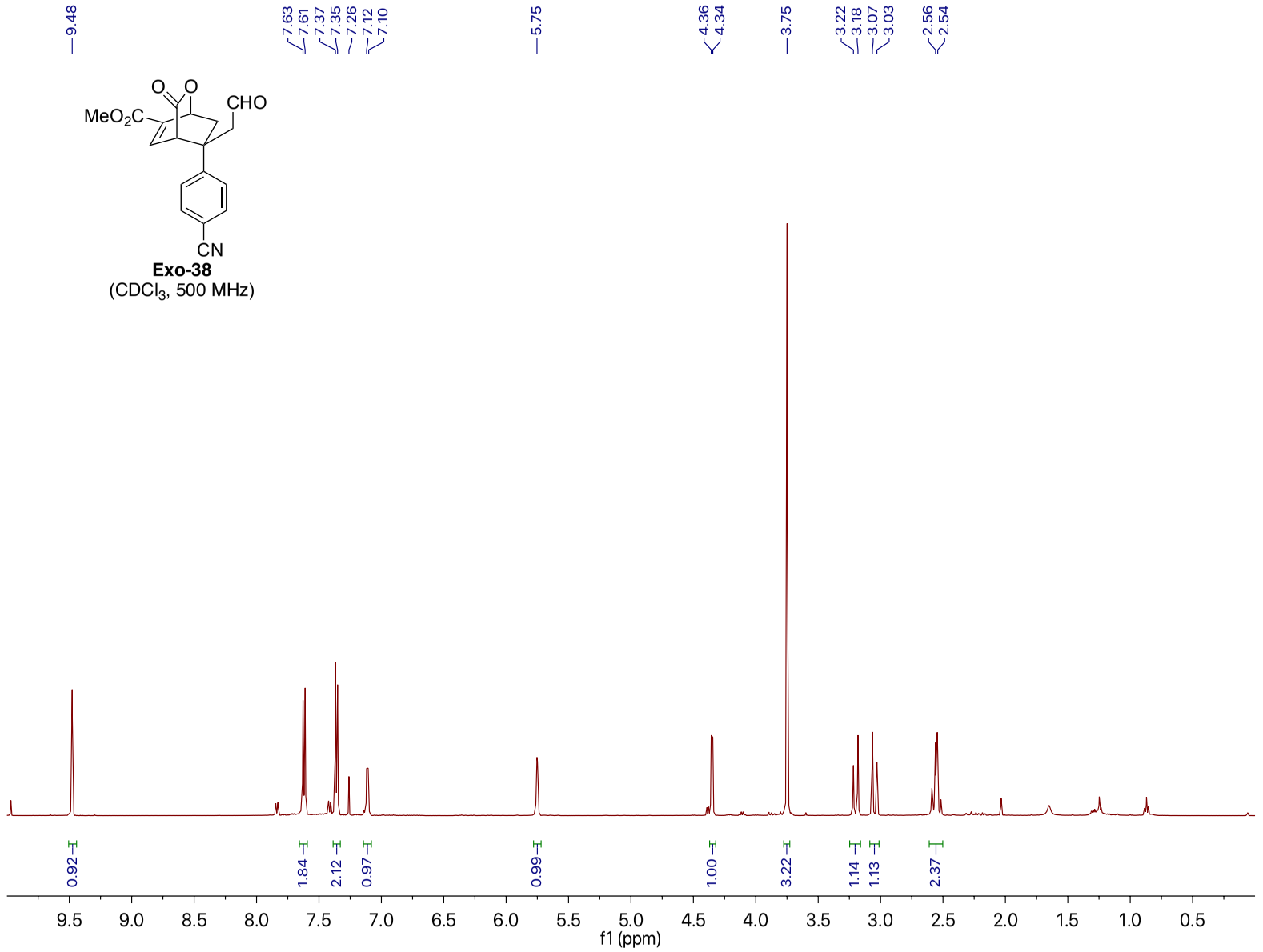

200.08
170.36
162.47
158.92
140.13
137.14
134.12
128.01
114.53
77.16
73.65
55.39
55.15
52.55
51.31
42.50
39.66
MeO
O
O
CO2Me
OHC
Endo-37
(CDCl3, 126 MHz)
f1 (ppm)

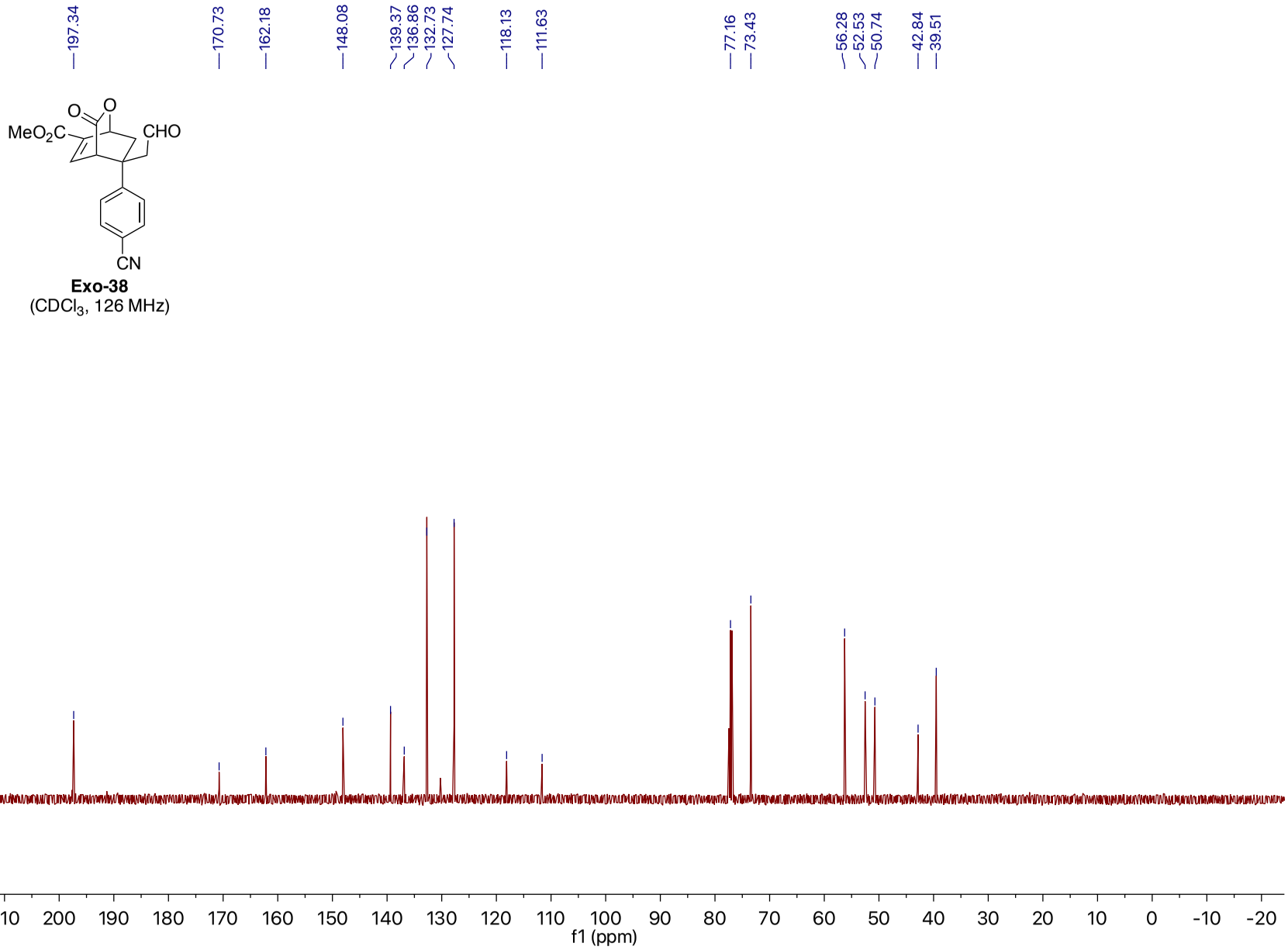

9.45
9.45
9.44
7.26
7.13
7.11
6.84
6.83
5.75
5.74
5.74
5.73
4.27
4.25
3.77
3.74
3.10
3.10
3.07
3.06
2.87
2.87
2.84
2.84
2.54
2.54
2.54
O
O
CHO
MeO2C
OMe
Exo-37
(CDCl3, 500 MHz)
0.77
2.98
1.94
0.91
1.02
3.09
2.87
1.01
1.00
f1 (ppm)

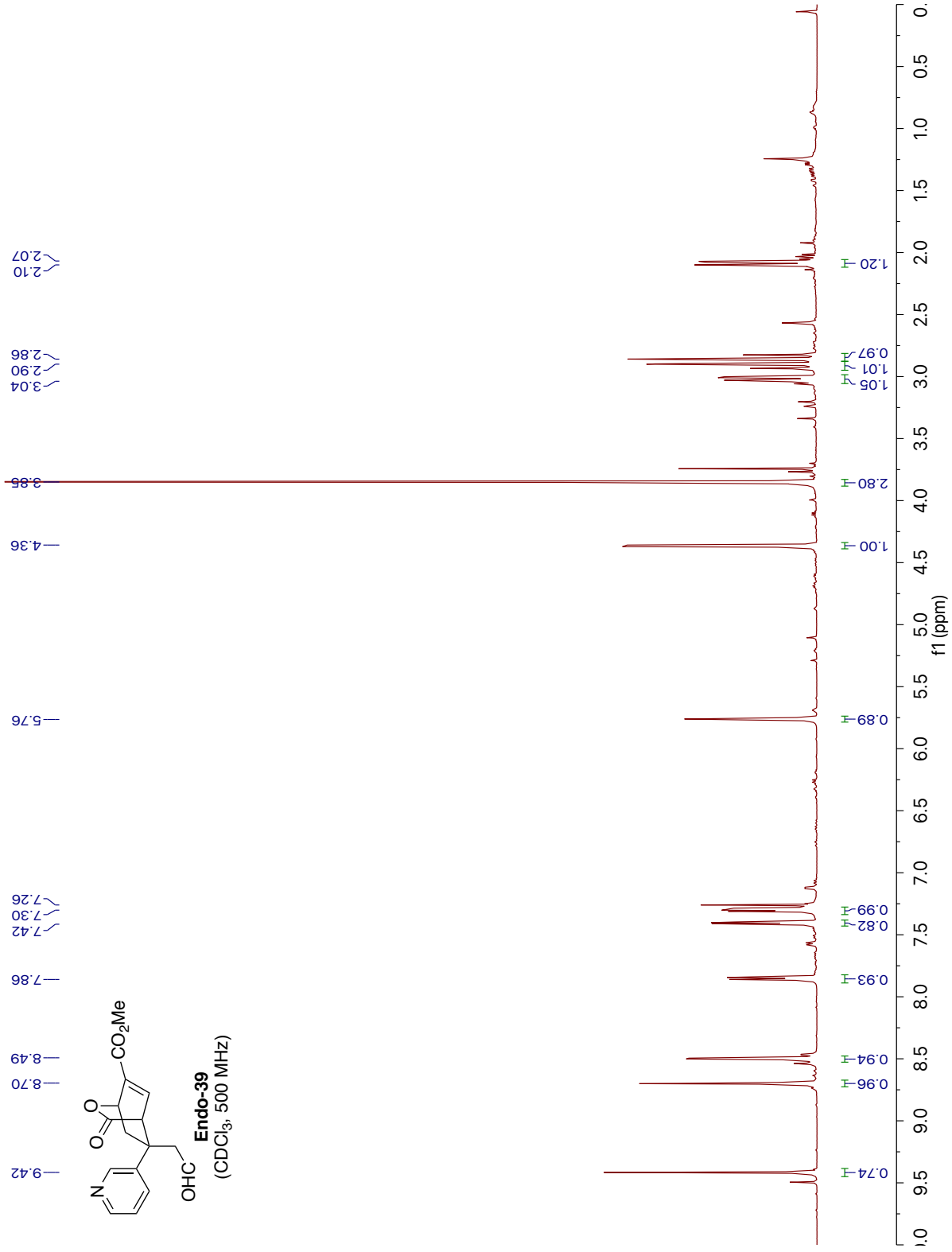

198.90
171.46
162.51
158.70
140.29
135.98
134.09
127.72
114.44
77.16
73.75
56.44
55.38
52.37
51.93
42.10
38.93
O
O
CHO
MeO2C
OMe
Exo-37
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

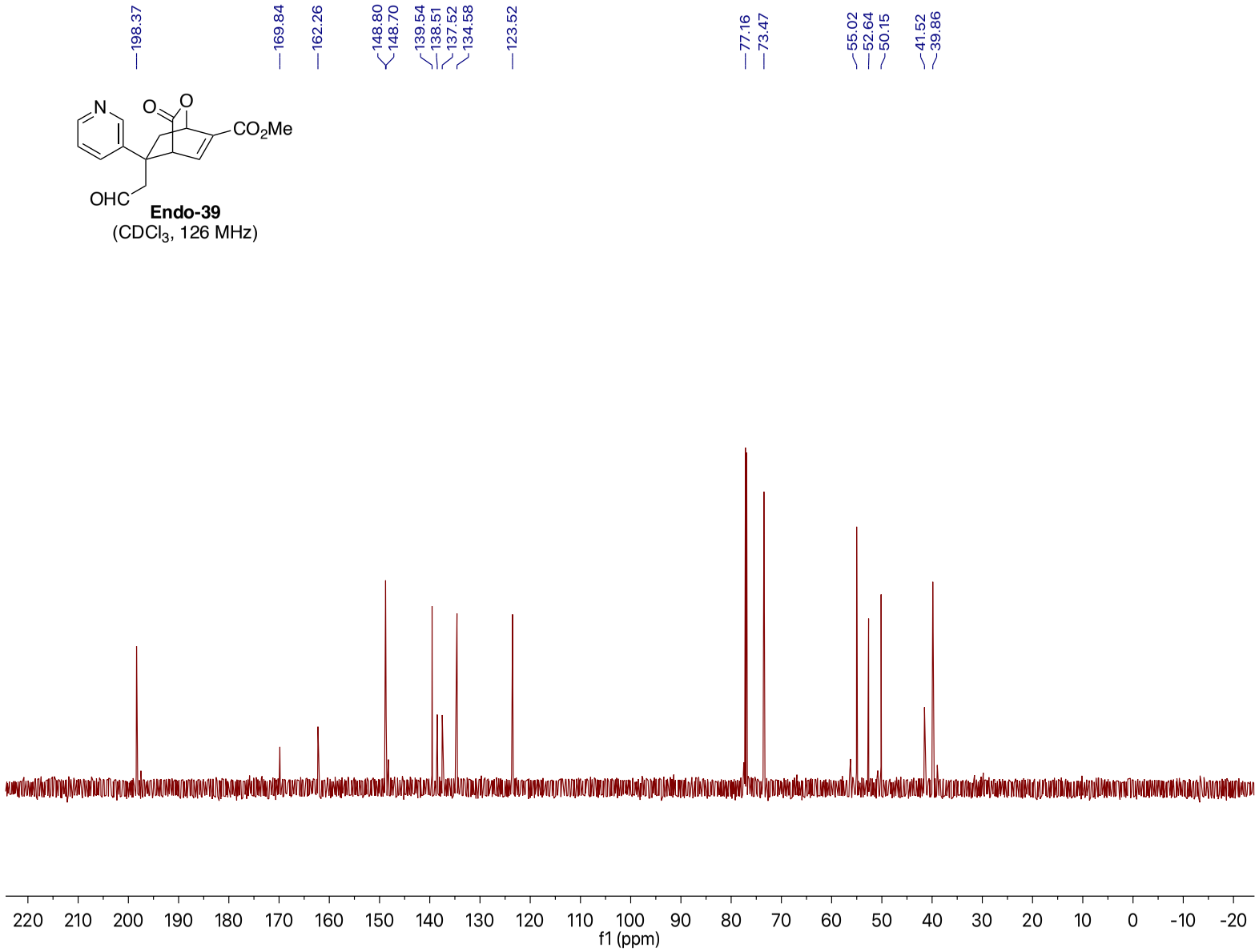

9.41
7.68
7.67
7.60
7.59
7.43
7.43
7.42
7.41
5.77
4.34
4.32
3.87
3.02
2.99
2.92
2.83
2.10
2.07
NC
O
O
CO2Me
OHC
Endo-38
(CDCl3, 500 MHz)
0.76
1.78
1.86
0.89
0.85
0.94
2.86
0.93
1.00
0.98
0.95
f1 (ppm)


198.12
169.78
162.19
147.97
139.47
137.60
132.74
127.89
118.20
111.81
77.16
73.44
54.88
52.65
50.27
43.09
39.99
NC
O
O
CO2Me
OHC
Endo-38
(CDCl3, 126 MHz)
S66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

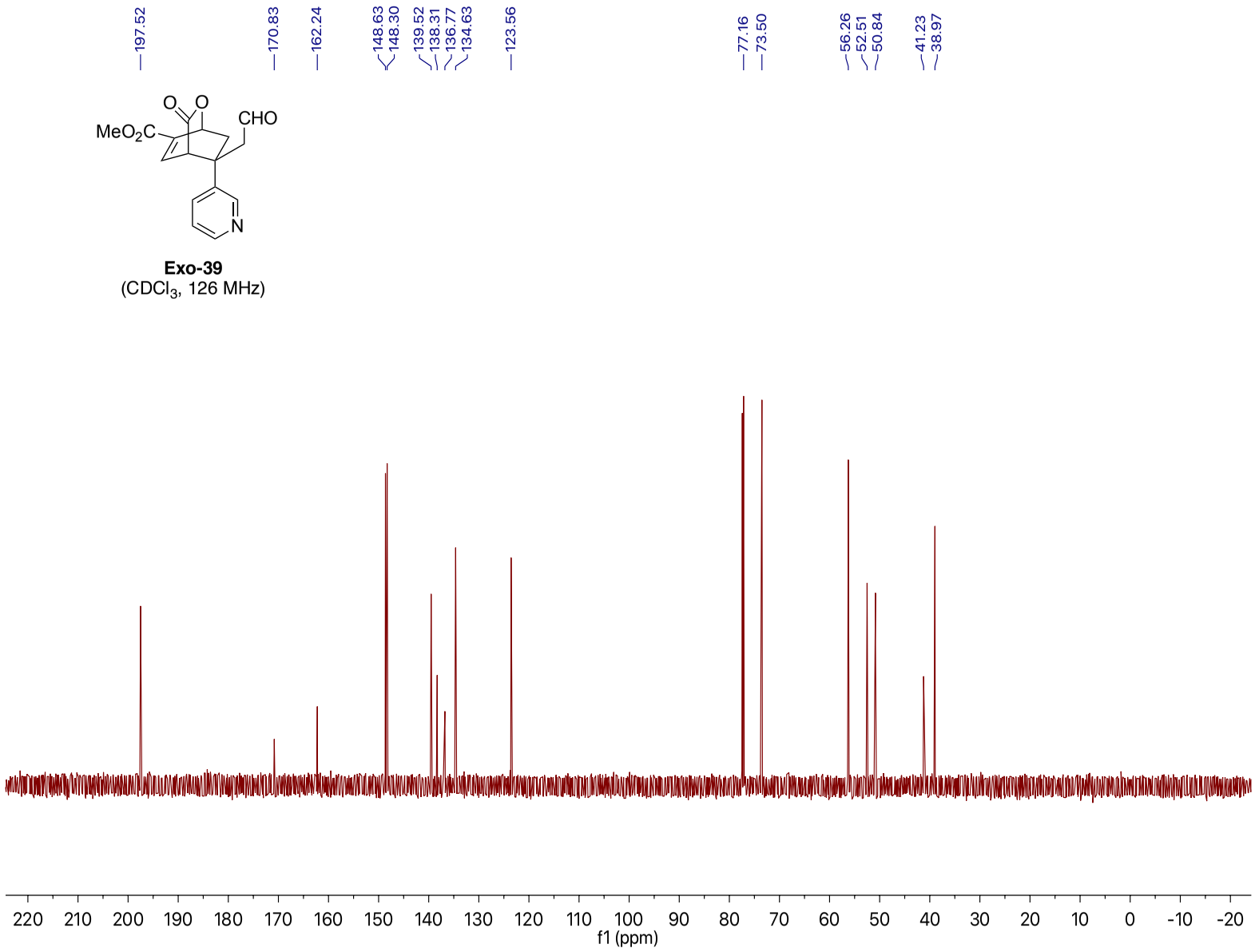

9.48
7.63
7.61
7.37
7.35
7.26
7.12
7.10
5.75
4.36
4.34
3.75
3.22
3.18
3.07
3.03
2.56
2.54
O
O
MeO2C
CHO
CN
Exo-38
(CDCl3, 500 MHz)
0.92
1.84
2.12
0.97
0.99
1.00
3.22
1.14
1.13
2.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

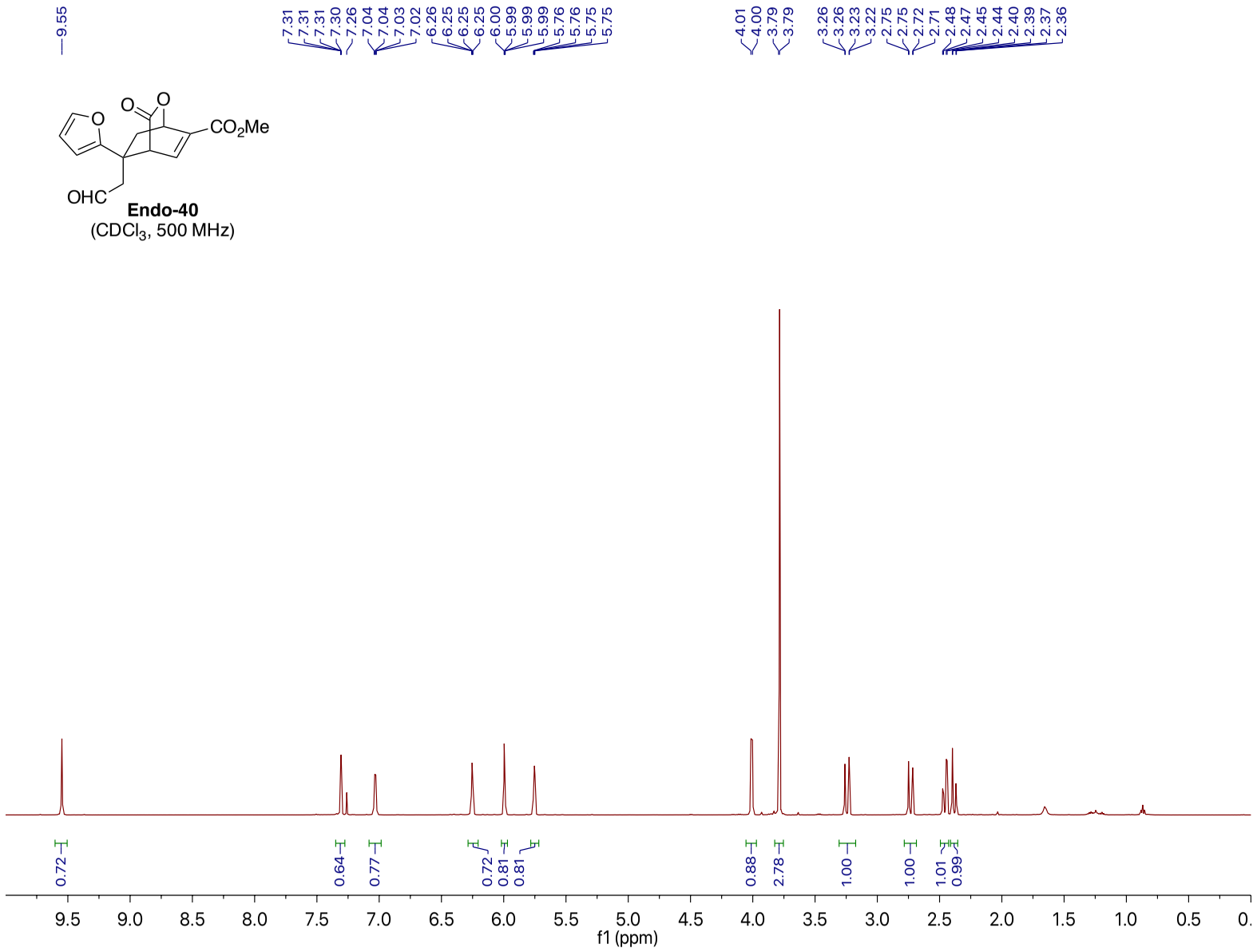

197.34
170.73
162.18
148.08
139.37
136.86
132.73
127.74
118.13
111.63
77.16
73.43
56.28
52.53
50.74
42.84
39.51
O
O
MeO2C
CHO
CN
Exo-38
(CDCl3, 126 MHz)
S68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

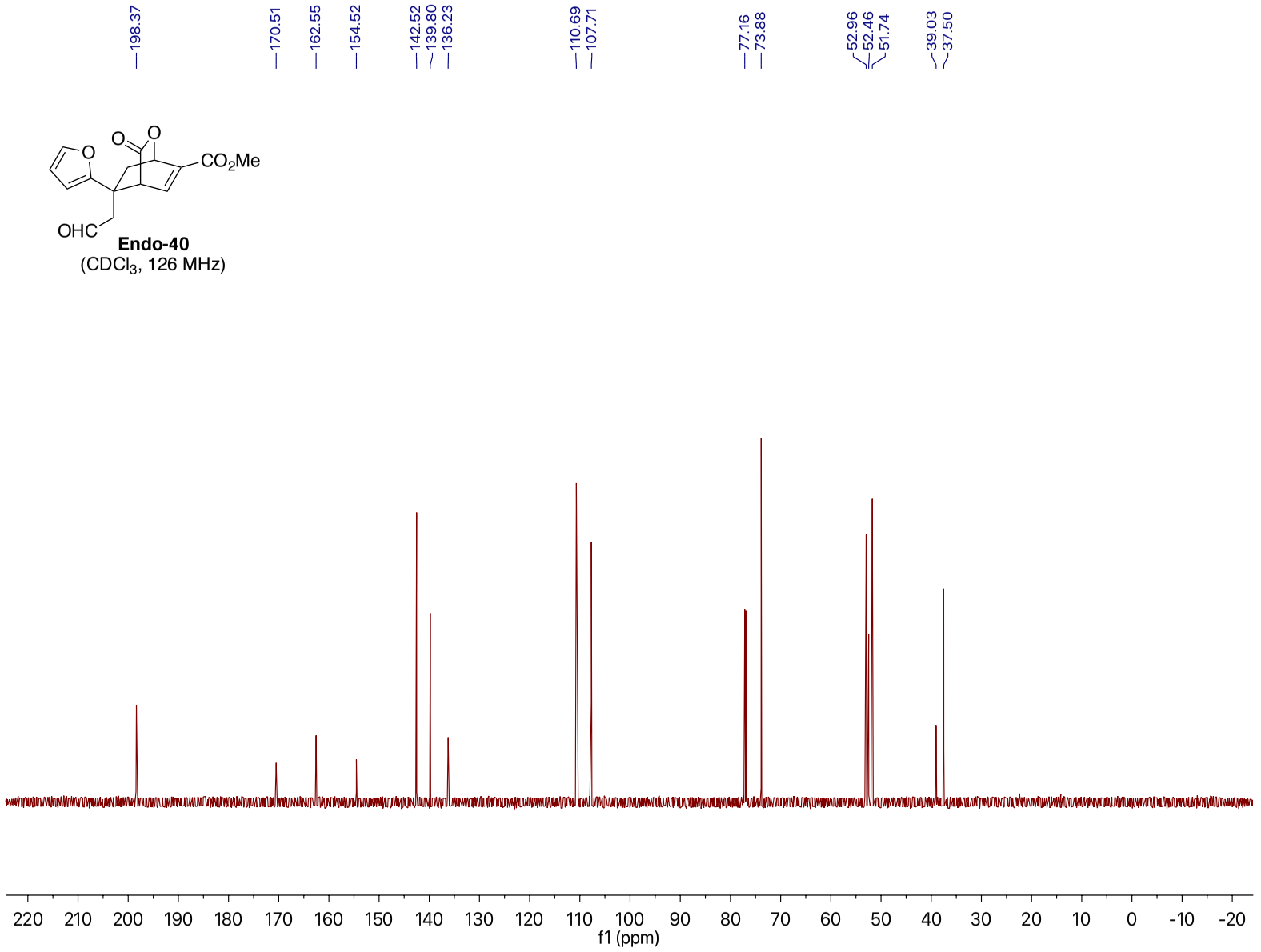

Endo-39
(CDCl3, 500 MHz)
CO2Me
OHC
O
O
N
9.42
8.70
8.49
7.86
7.42
7.30
7.26
5.76
4.36
3.85
3.04
2.90
2.86
2.10
2.07
0.74
0.96
0.94
0.93
0.99
0.82
0.89
1.00
2.80
1.05
1.01
0.97
1.20
f1 (ppm)

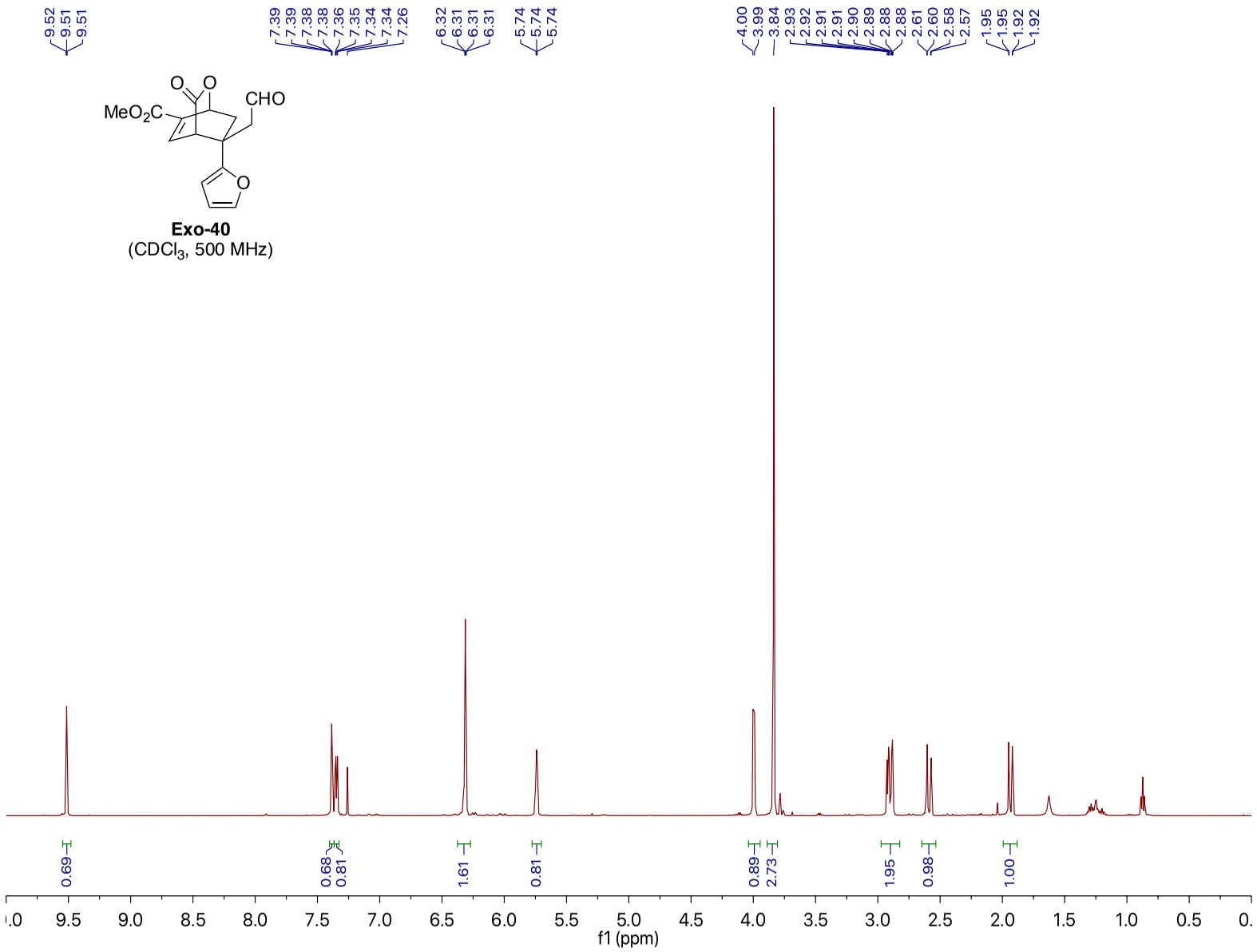

198.37
169.84
162.26
148.80
148.70
139.54
138.51
137.52
134.58
123.52
77.16
73.47
55.02
52.64
50.15
41.52
39.86
N
O
O
CO2Me
OHC
Endo-39
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

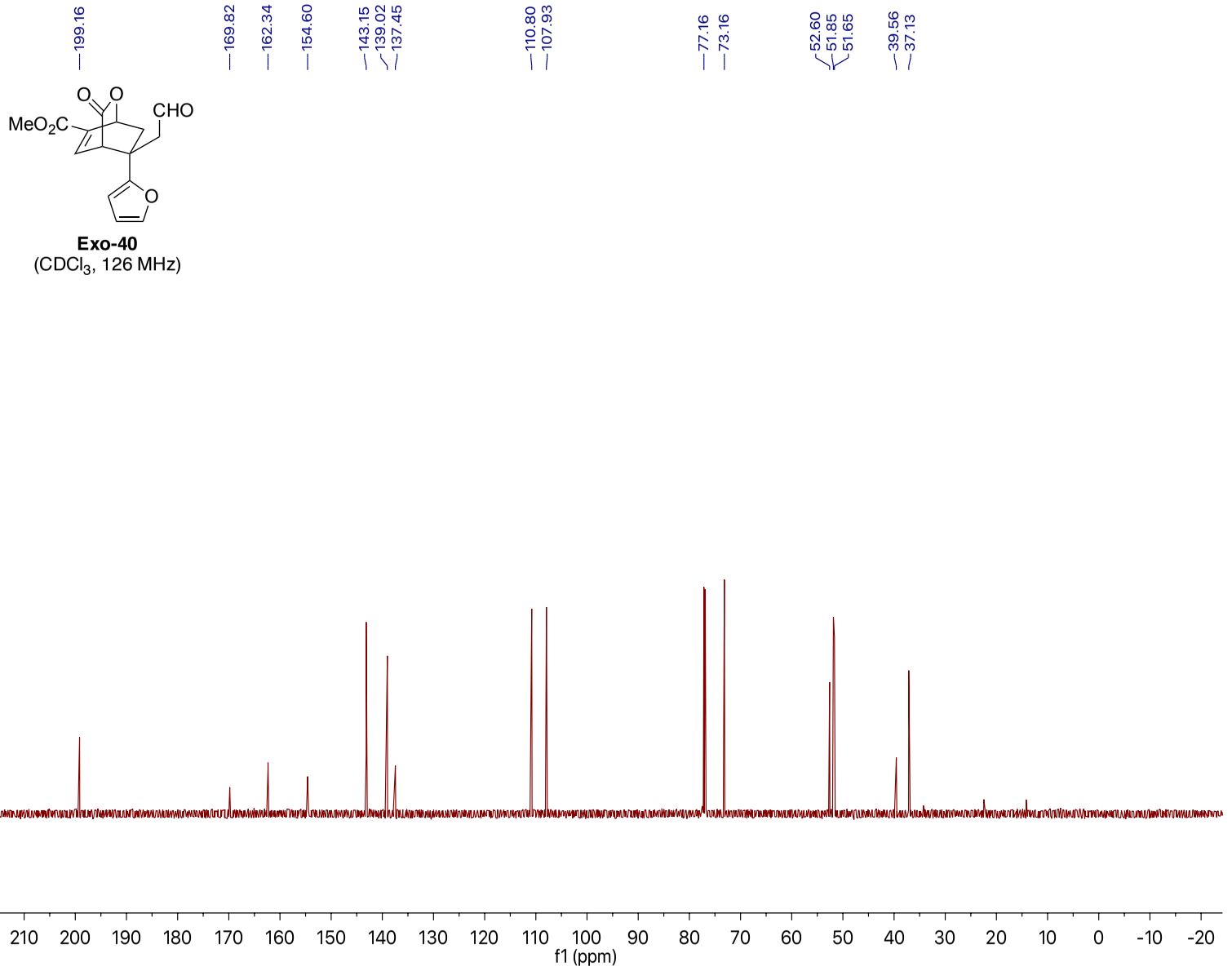
9.50
8.54
8.46
7.58
7.26
7.12
5.76
4.37
4.36
3.75
3.25
3.21
3.06
3.03
2.57
0.78
1.05
0.89
1.03
1.21
0.83
0.90
1.00
3.04
1.05
1.05
1.96
CHO
O
O
MeO2C
N
Exo-39
(CDCl3, 500 MHz)
f1 (ppm)


197.52
170.83
162.24
148.63
148.30
139.52
138.31
136.77
134.63
123.56
77.16
73.50
56.26
52.51
50.84
41.23
38.97
O
O
CHO
MeO2C
N
Exo-39
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

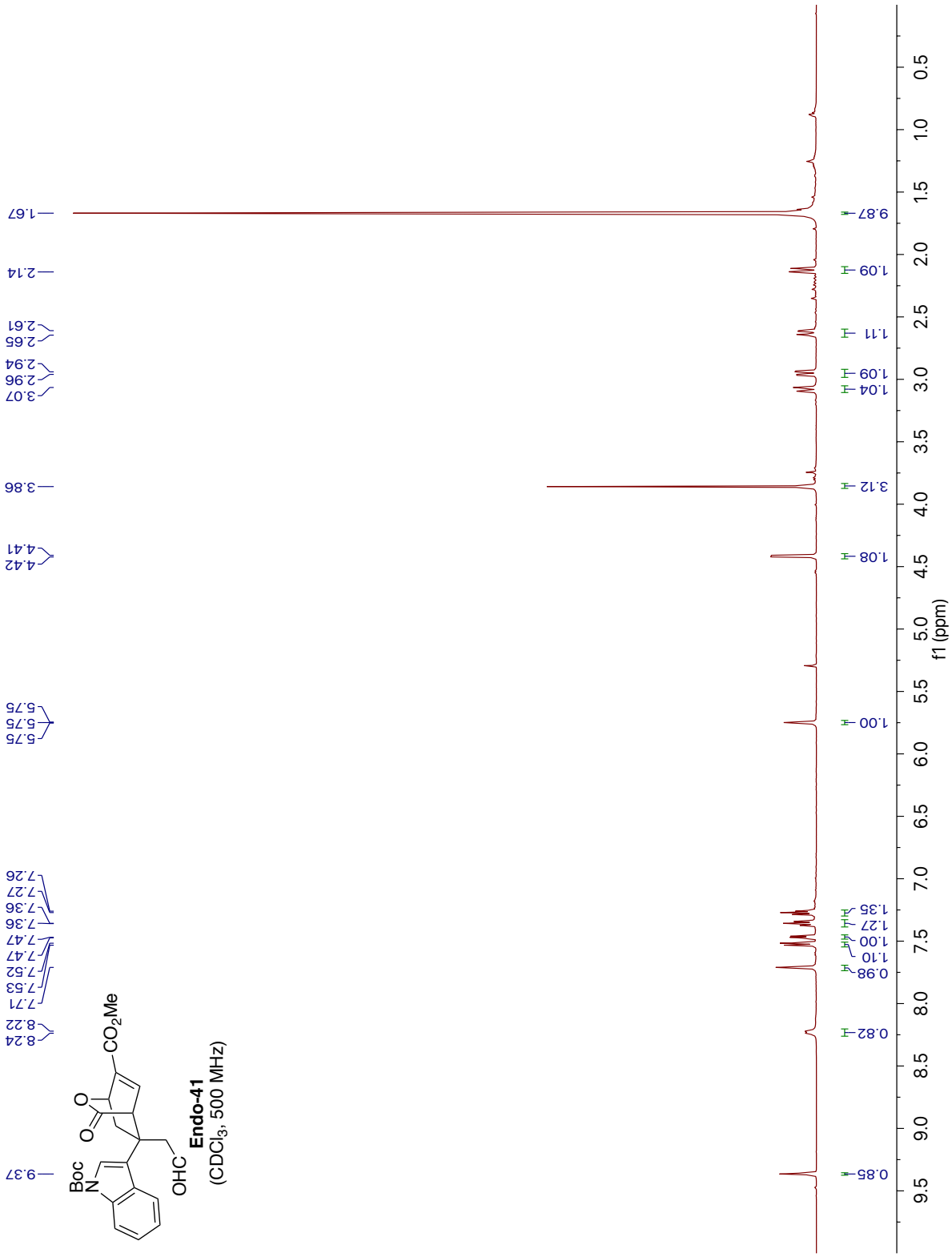

9.55
7.31
7.31
7.31
7.30
7.26
7.04
7.04
7.03
7.02
6.26
6.25
6.25
6.25
6.00
5.99
5.99
5.99
5.76
5.76
5.75
5.75
4.01
4.00
3.79
3.79
3.26
3.26
3.23
3.22
2.75
2.75
2.72
2.71
2.48
2.47
2.45
2.44
2.40
2.39
2.37
2.36
O
O
O
CO2Me
OHC
Endo-40
(CDCl3, 500 MHz)
0.72
0.64
0.77
0.72
0.81
0.81
0.88
2.78
1.00
1.00
1.01
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

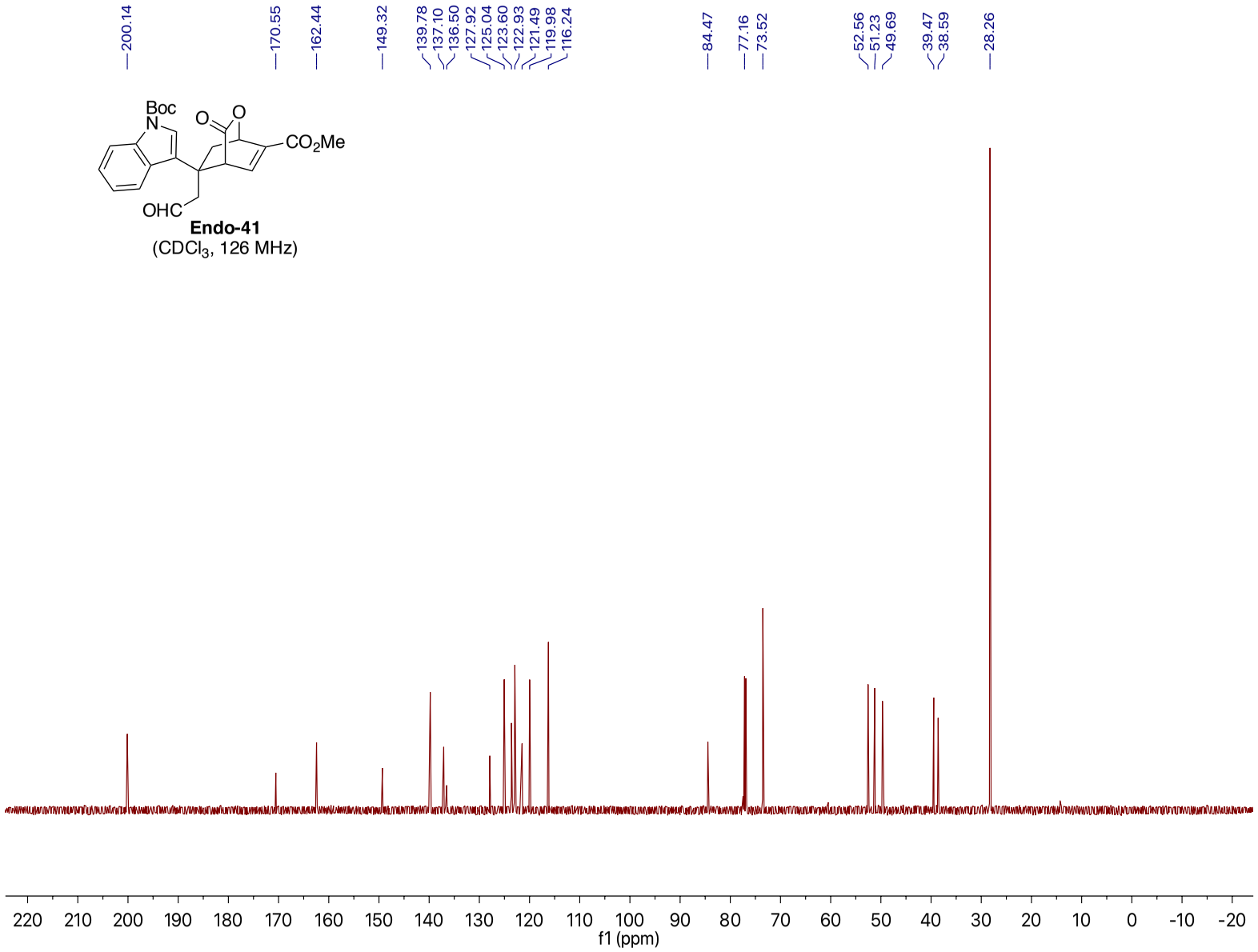

198.37
170.51
162.55
154.52
142.52
139.80
136.23
110.69
107.71
77.16
73.88
52.96
52.46
51.74
39.03
37.50
O
O
O
CO2Me
OHC
Endo-40
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

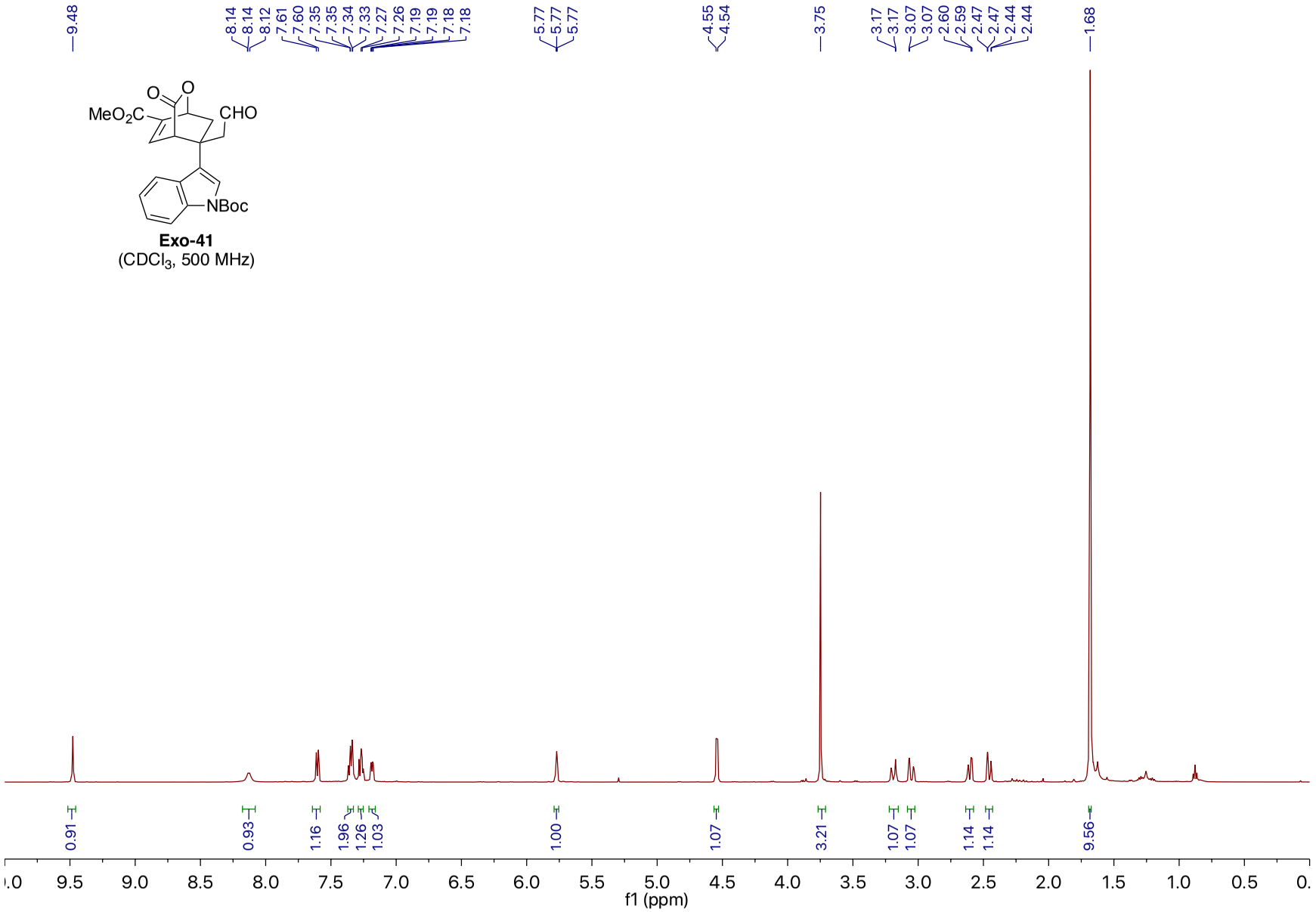

9.52
9.51
9.51
7.39
7.39
7.38
7.38
7.36
7.35
7.34
7.34
7.26
6.32
6.31
6.31
6.31
5.74
5.74
5.74
4.00
3.99
3.84
2.93
2.92
2.91
2.91
2.90
2.89
2.88
2.88
2.61
2.60
2.58
2.57
1.95
1.95
1.92
1.92
O
O
CHO
MeO2C
O
Exo-40
(CDCl3, 500 MHz)
0.69
0.68
0.81
1.61
0.81
0.89
2.73
1.95
0.98
1.00
f1 (ppm)

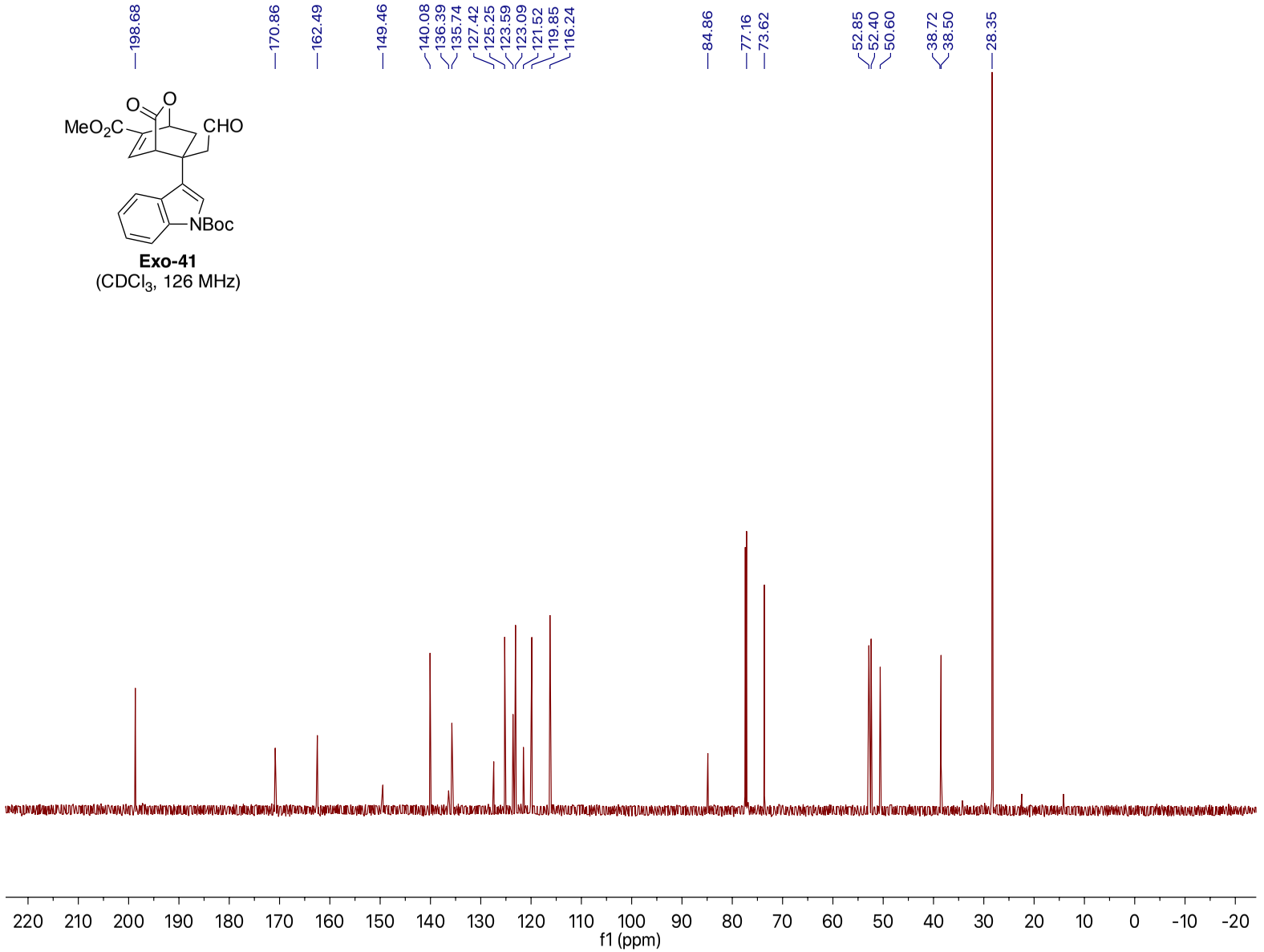


Exo-40
($CDCl_3$, 126 MHz)

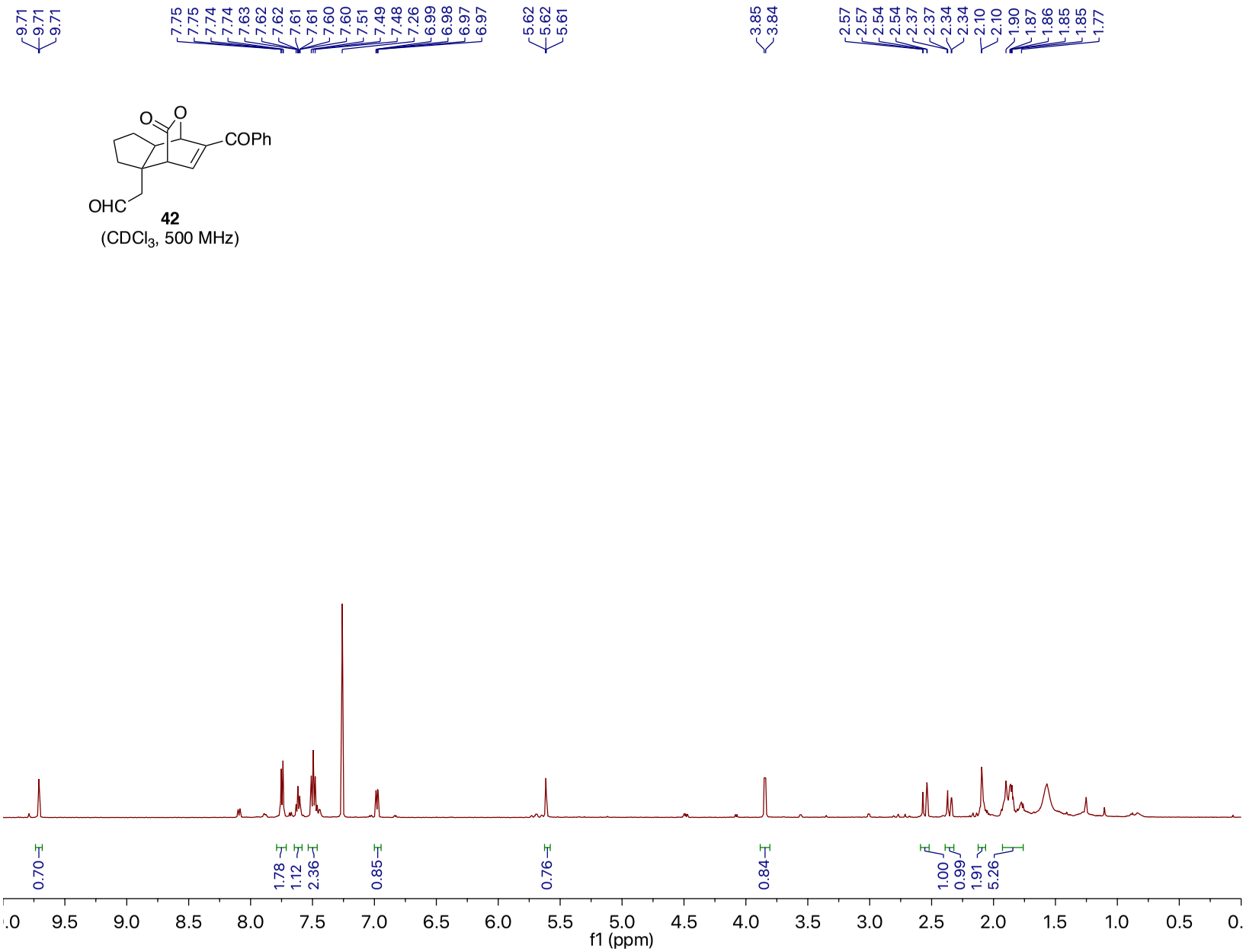

Endo-41
(CDCl3, 500 MHz)
Boc
N
O
O
CO2Me
OHC
f1 (ppm)

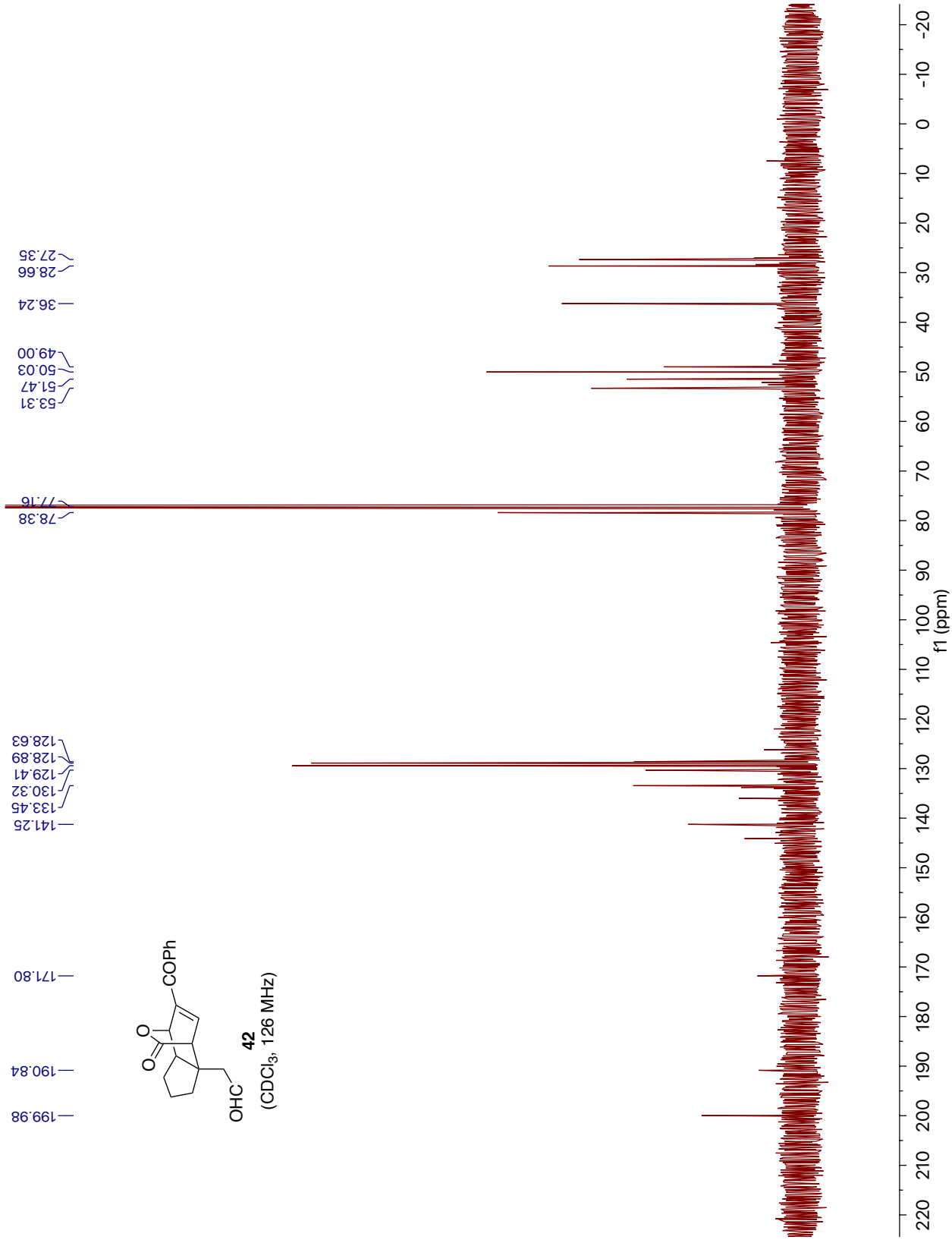

200.14
170.55
162.44
149.32
139.78
137.10
136.50
127.92
125.04
123.60
122.93
121.49
119.98
116.24
84.47
77.16
73.52
52.56
51.23
49.69
39.47
38.59
28.26
Boc
N
O
O
CO2Me
OHC
Endo-41
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

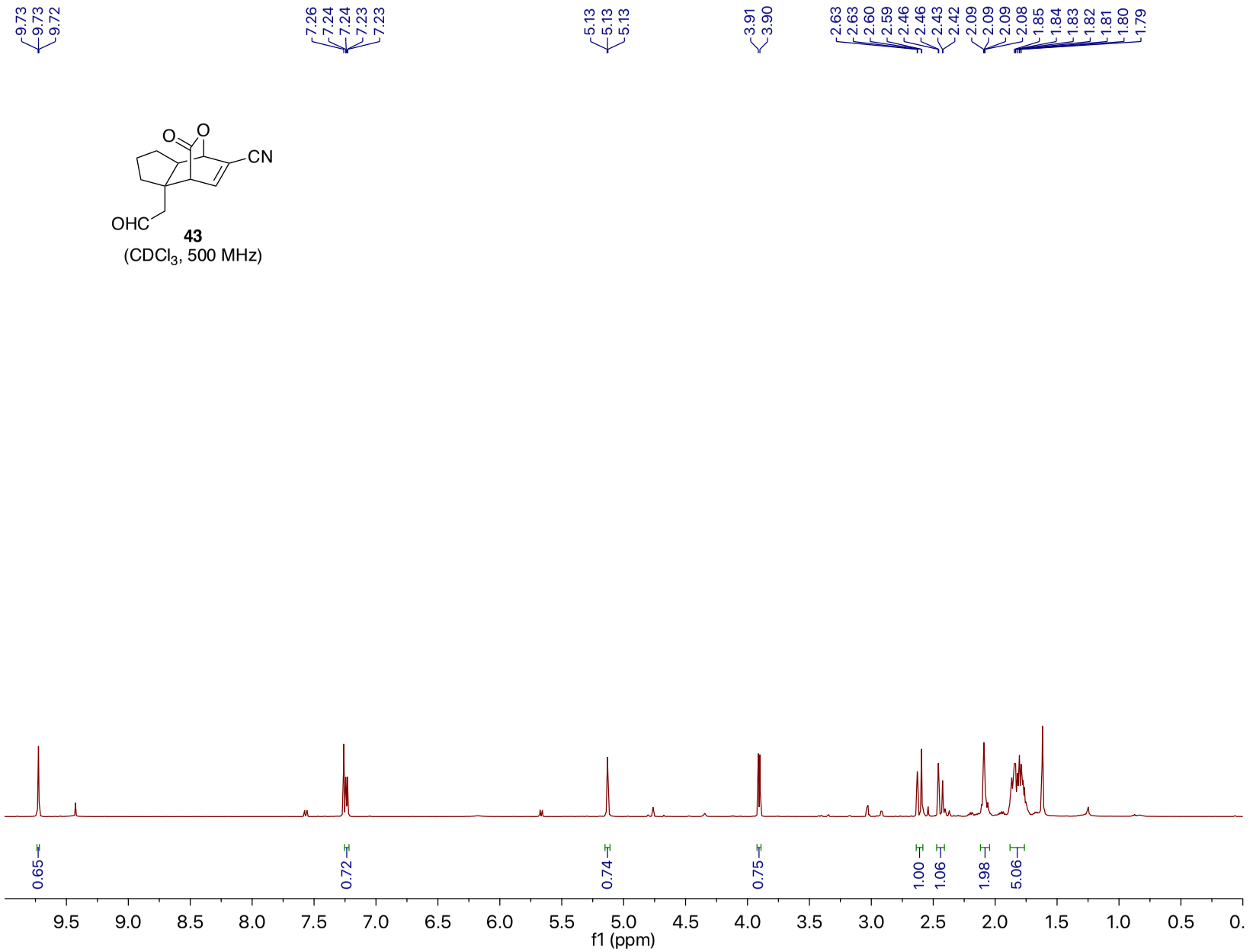

9.48
8.14
8.14
8.12
7.61
7.60
7.35
7.35
7.34
7.33
7.27
7.26
7.19
7.19
7.18
7.18
5.77
5.77
5.77
4.55
4.54
3.75
3.17
3.17
3.07
3.07
2.60
2.59
2.47
2.47
2.44
2.44
1.68
O
O
MeO2C
CHO
NBoc
Exo-41
(CDCl3, 500 MHz)
0.91
0.93
1.16
1.96
1.26
1.03
1.00
1.07
3.21
1.07
1.07
1.14
1.14
9.56
f1 (ppm)

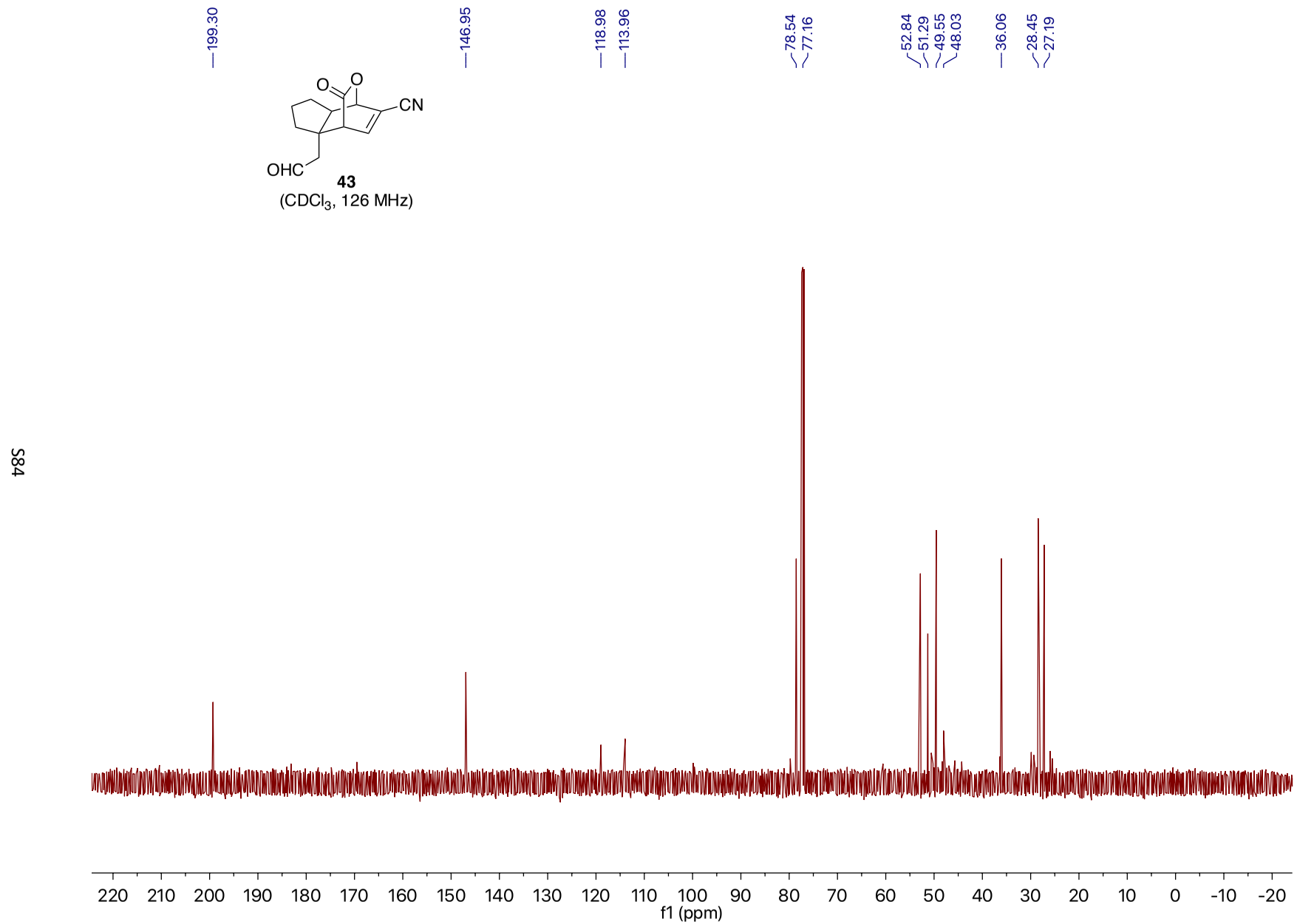


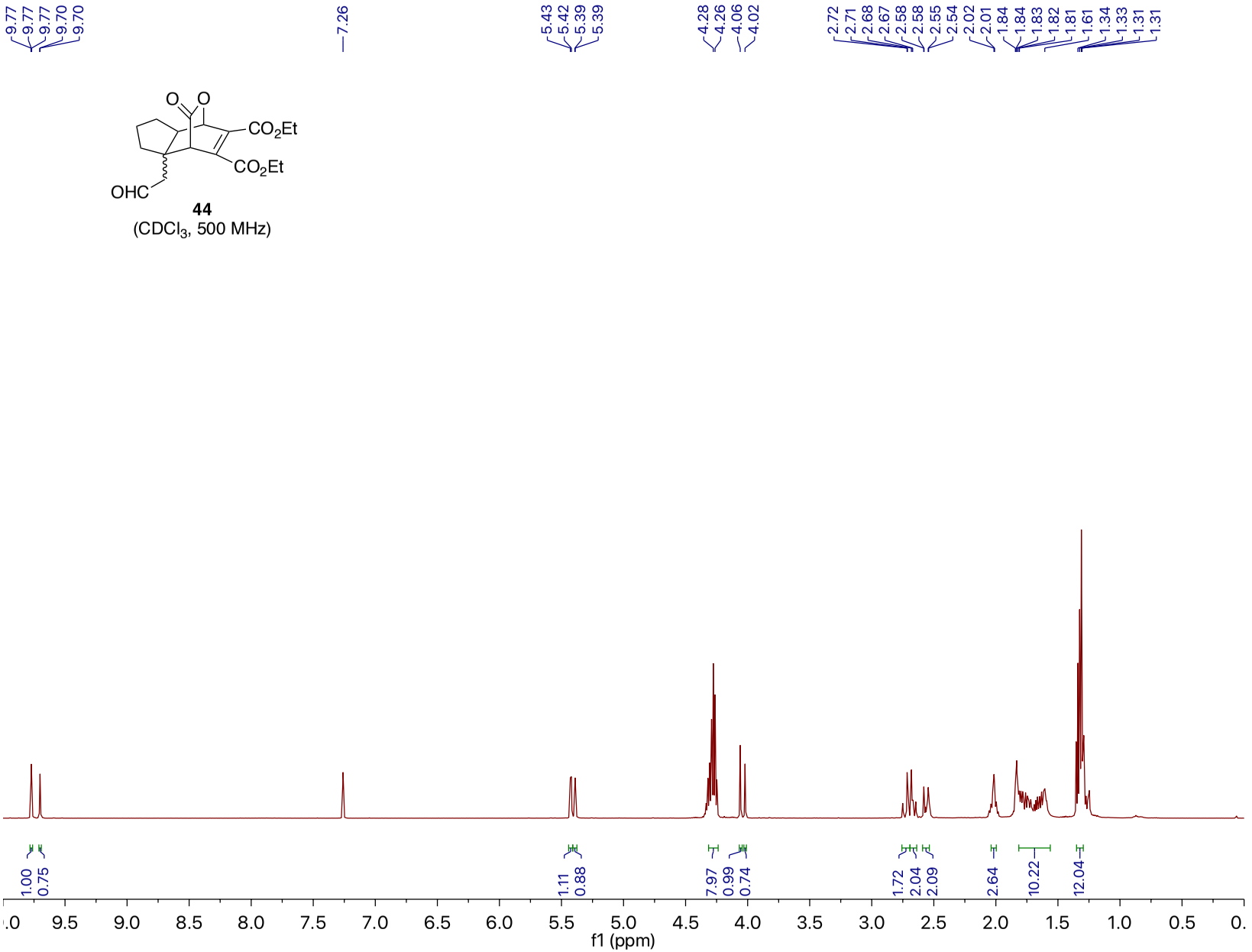
Exo-41
($CDCl_3$, 126 MHz)

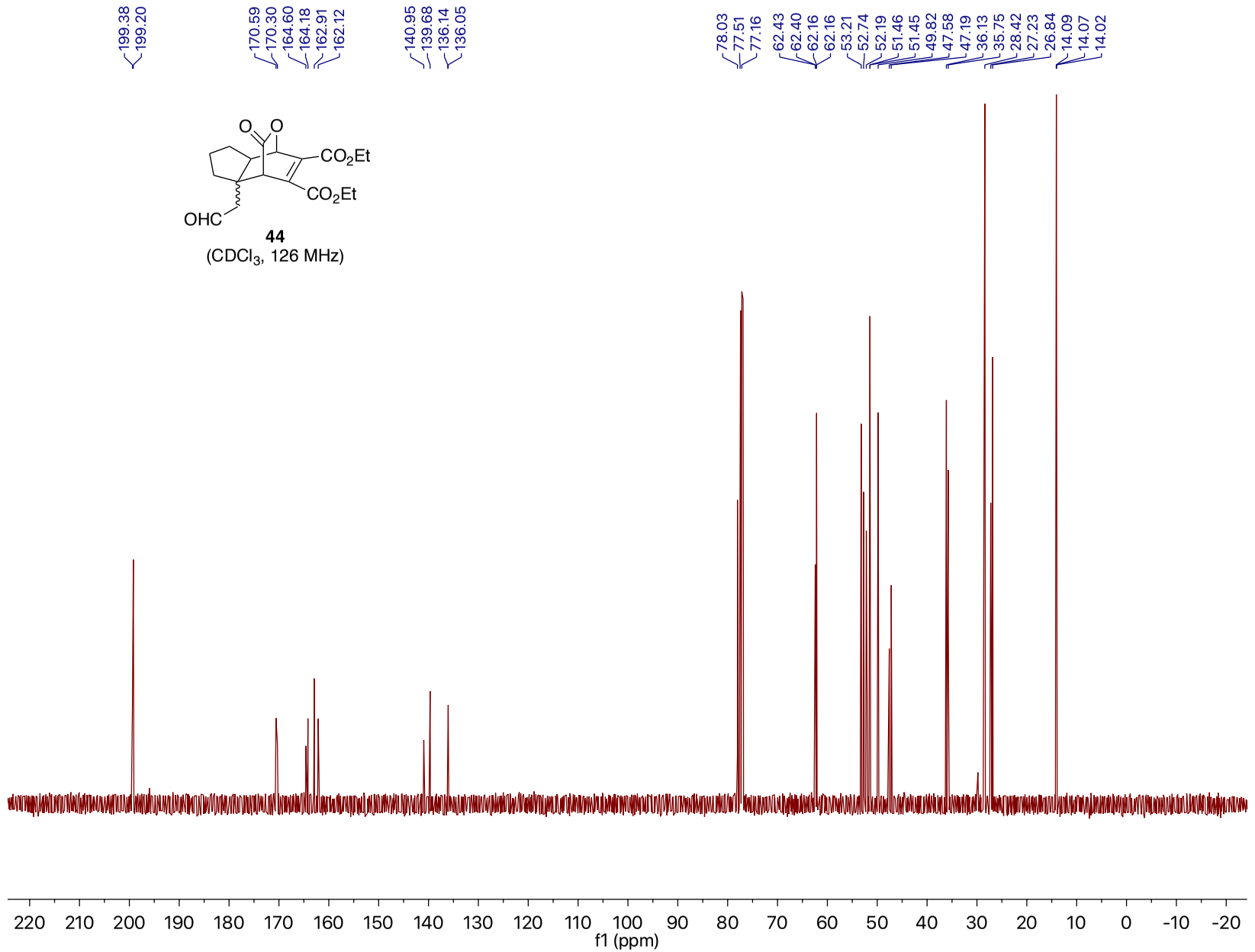

9.71
9.71
9.71
7.75
7.75
7.74
7.74
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.51
7.49
7.48
7.26
6.99
6.98
6.97
6.97
5.62
5.62
5.61
3.85
3.84
2.57
2.57
2.54
2.54
2.37
2.37
2.34
2.34
2.10
2.10
1.90
1.87
1.86
1.85
1.85
1.77
O
O
COPh
OHC
42
(CDCl3, 500 MHz)
0.70
1.78
1.12
2.36
0.85
0.76
0.84
1.00
0.99
1.91
5.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


199.98
190.84
171.80
141.25
133.45
130.32
129.41
128.89
128.63
78.38
77.16
53.31
51.47
50.03
49.00
36.24
28.66
27.35
COPh
O
O
OHC
42
(CDCl3, 126 MHz)
f1 (ppm)

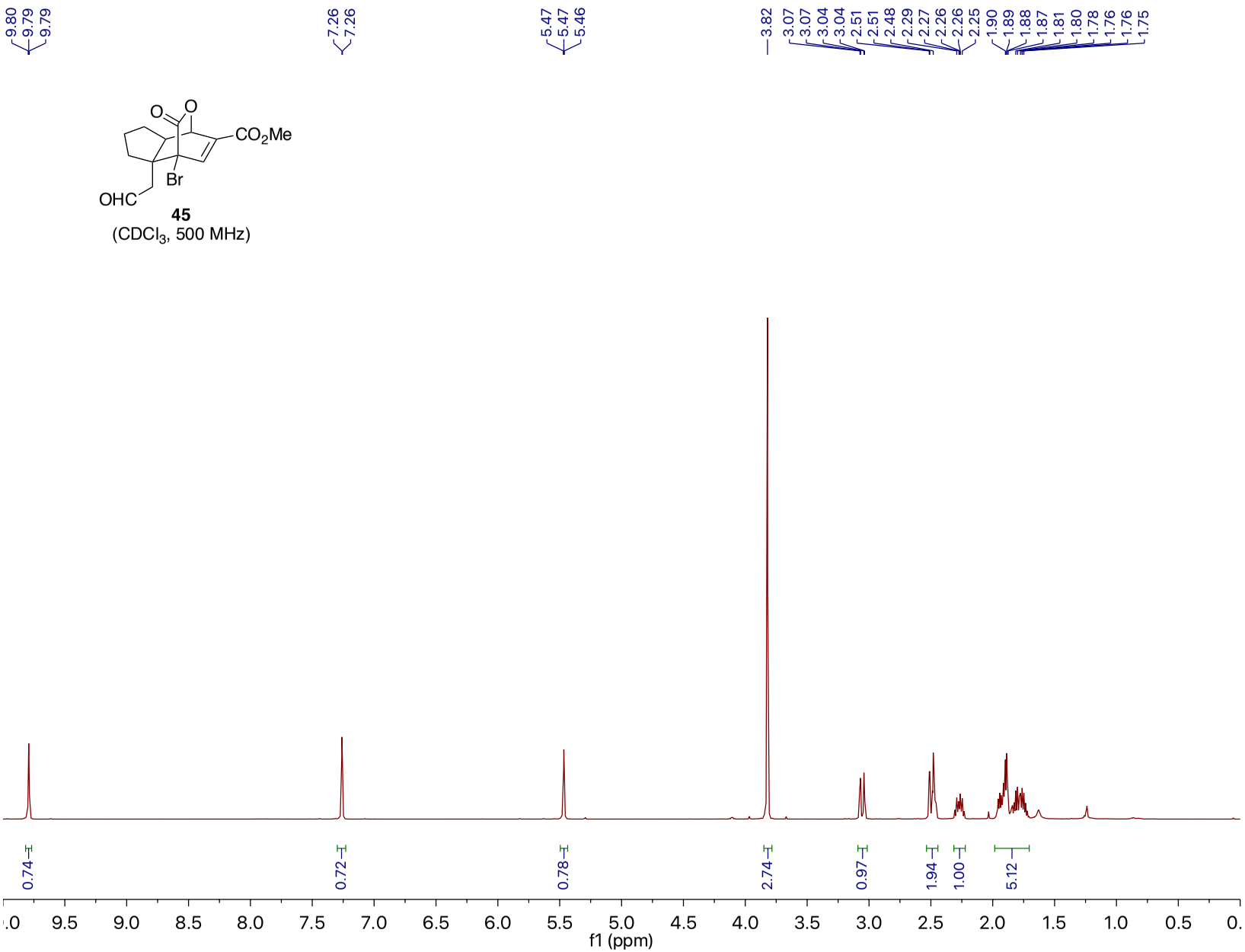

9.73
9.73
9.72
7.26
7.24
7.24
7.23
7.23
5.13
5.13
5.13
3.91
3.90
2.63
2.63
2.60
2.59
2.46
2.46
2.43
2.42
2.09
2.09
2.09
2.08
1.85
1.84
1.83
1.82
1.81
1.80
1.79
O
O
CN
OHC
43
(CDCl3, 500 MHz)
0.65
0.72
0.74
0.75
1.00
1.06
1.98
5.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

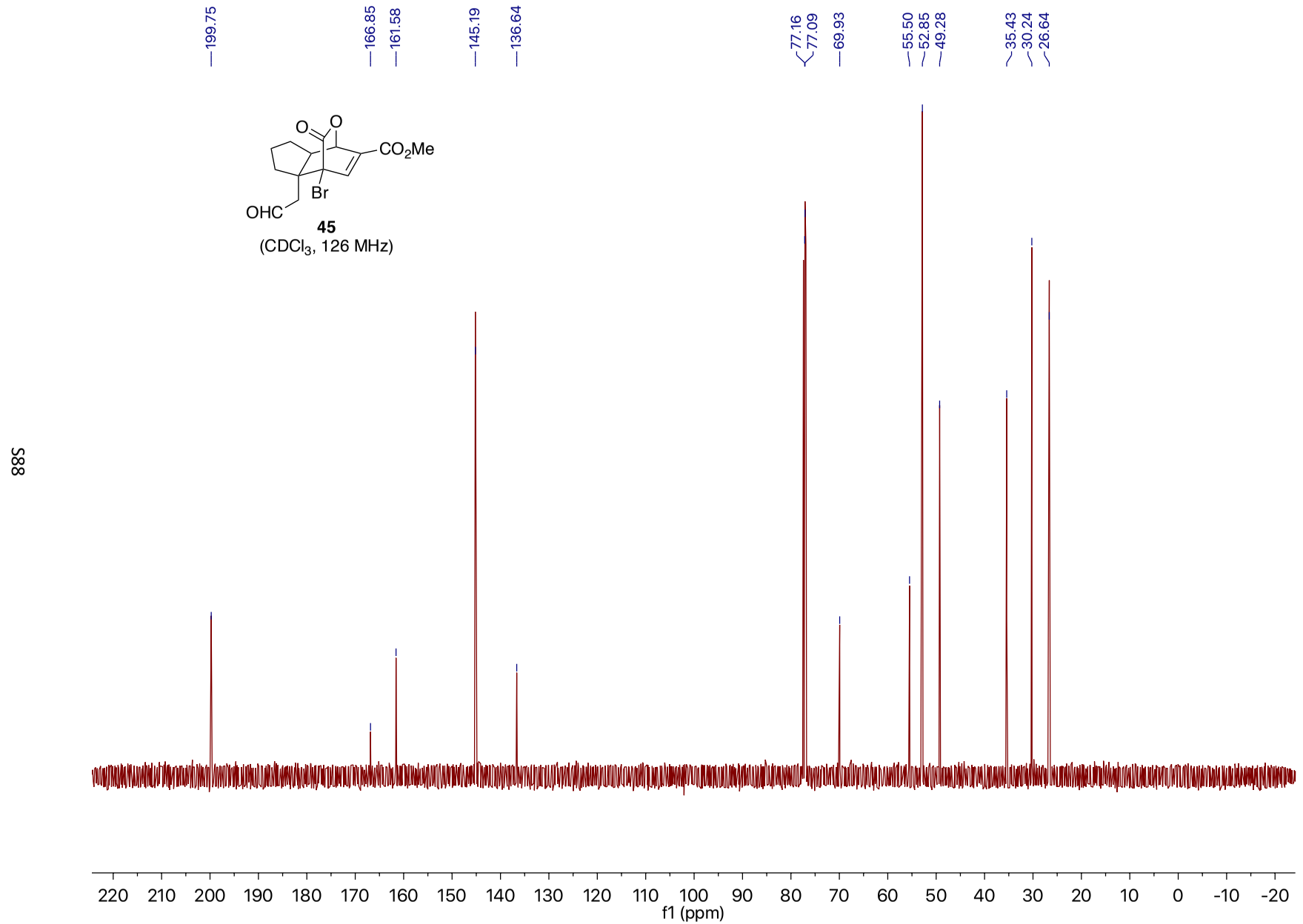

199.30
146.95
118.98
113.96
78.54
77.16
52.84
51.29
49.55
48.03
36.06
28.45
27.19
O
O
CN
OHC
43
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

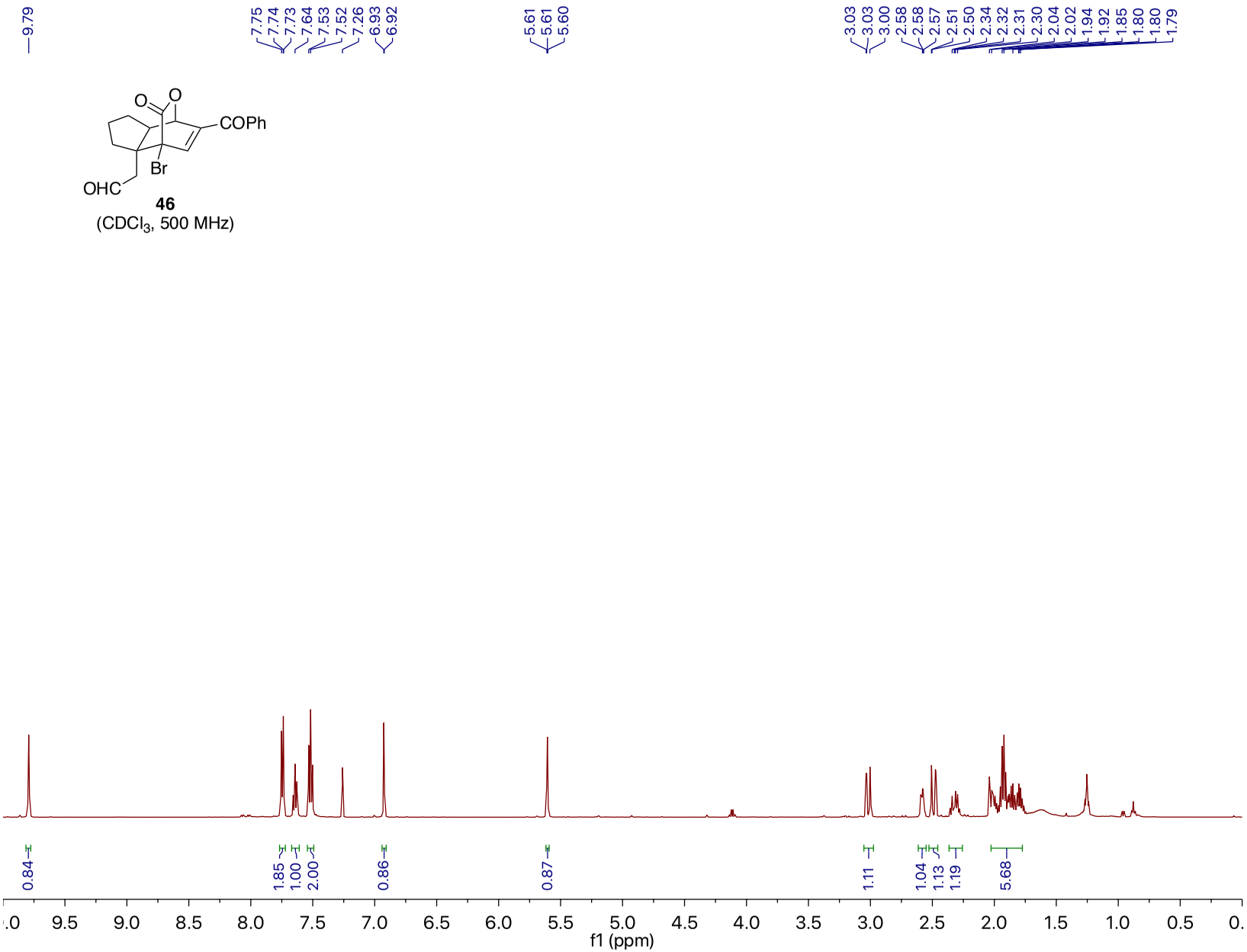

9.77
9.77
9.77
9.70
9.70
7.26
5.43
5.42
5.39
5.39
4.28
4.26
4.06
4.02
2.72
2.71
2.68
2.67
2.58
2.58
2.55
2.54
2.02
2.01
1.84
1.84
1.83
1.82
1.81
1.61
1.34
1.33
1.31
1.31
O
O
CO2Et
CO2Et
OHC
44
(CDCl3, 500 MHz)
1.00
0.75
1.11
0.88
7.97
0.99
0.74
1.72
2.04
2.09
2.64
10.22
12.04
f1 (ppm)

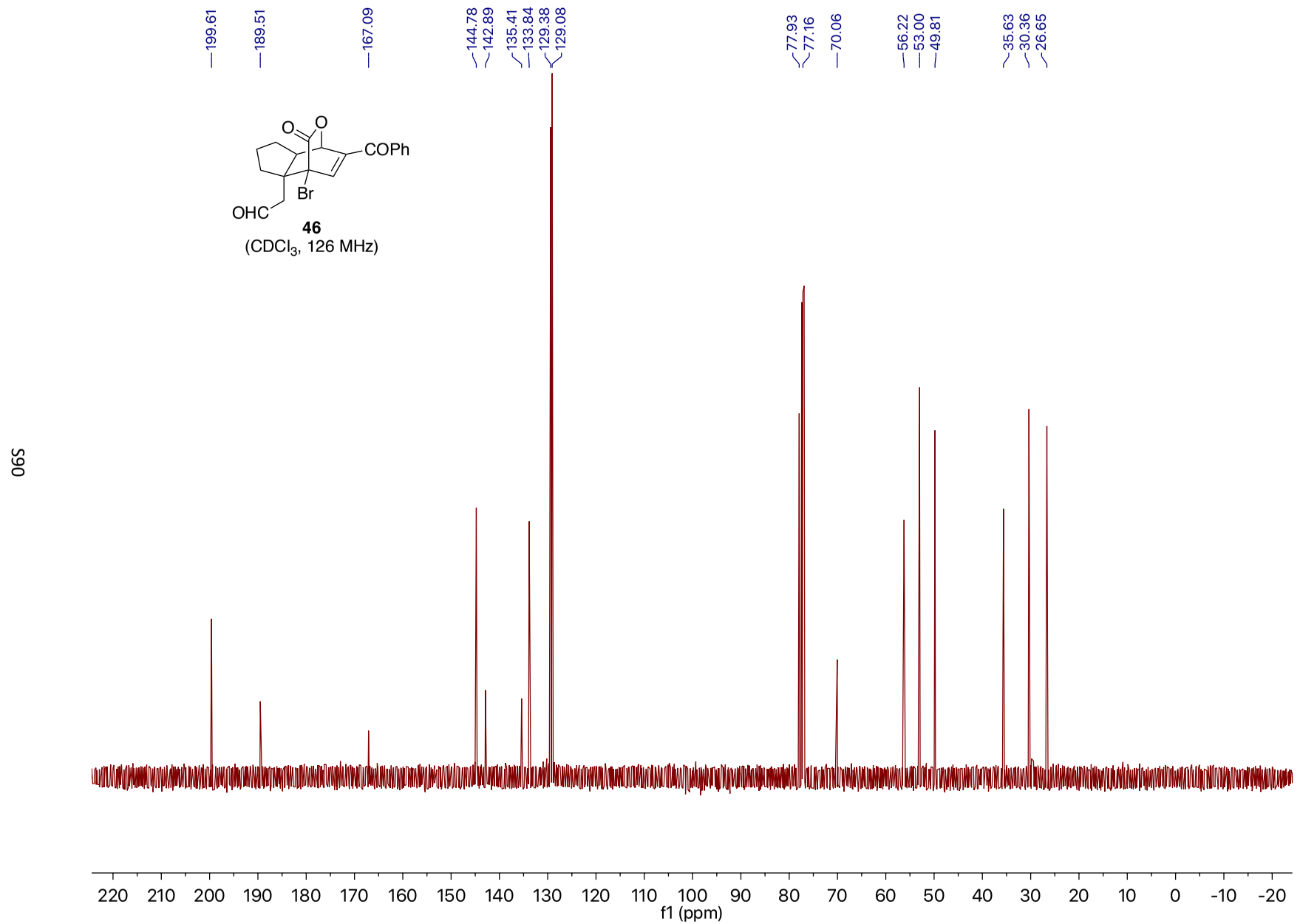


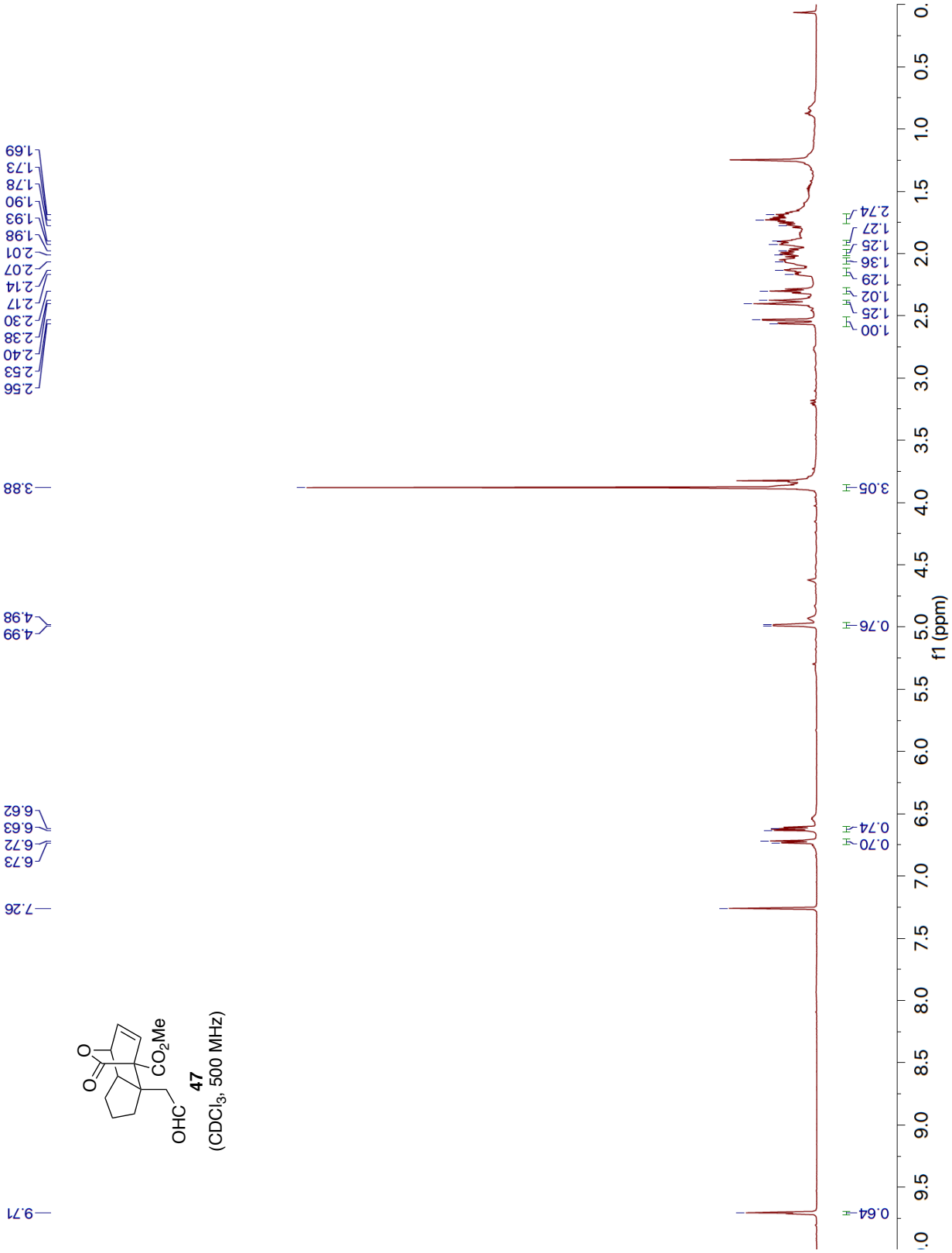
44
($CDCl_3$, 126 MHz)

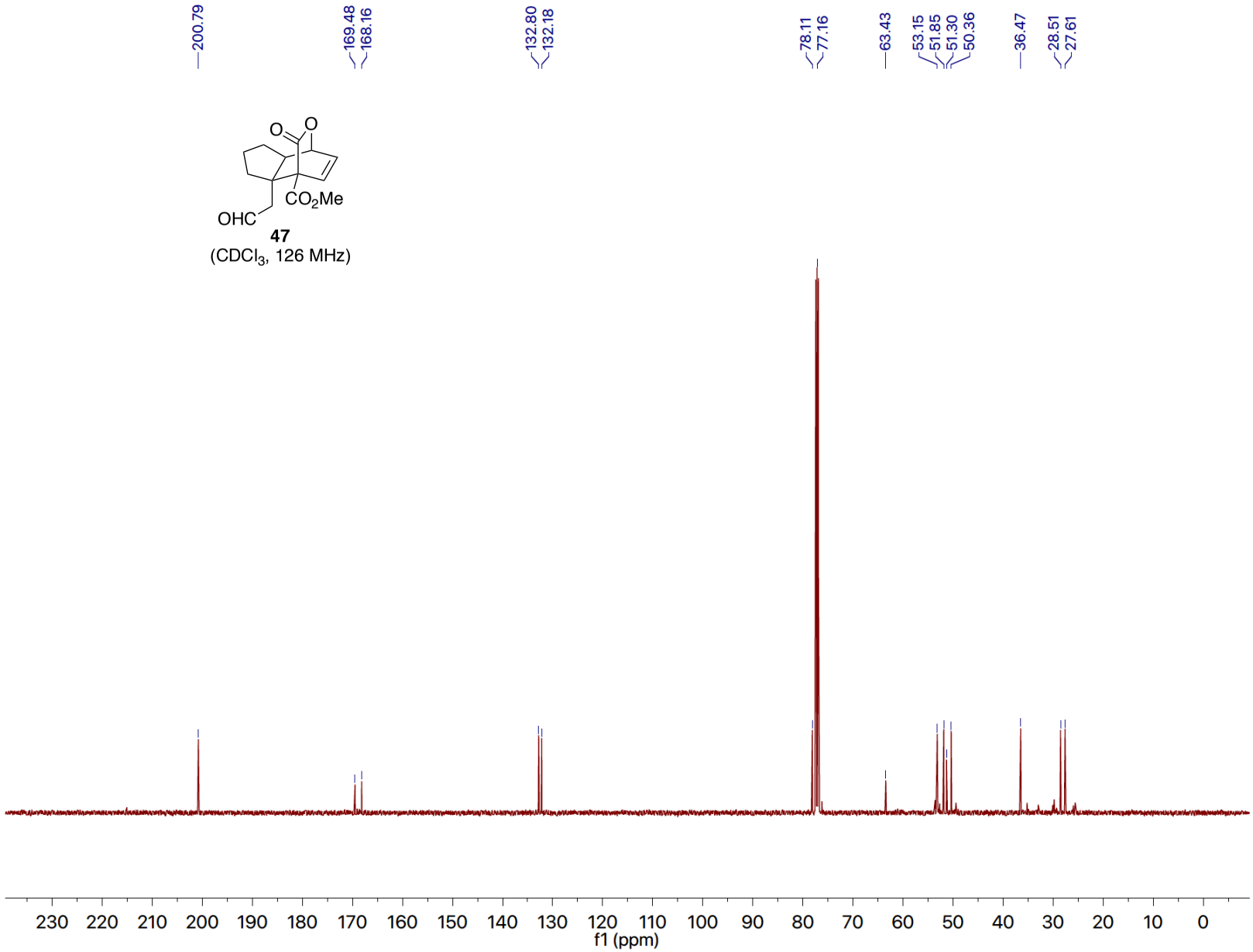

9.80
9.79
9.79
7.26
7.26
5.47
5.47
5.46
3.82
3.07
3.07
3.04
3.04
2.51
2.51
2.48
2.29
2.27
2.26
2.26
2.25
1.90
1.89
1.88
1.87
1.81
1.80
1.78
1.76
1.76
1.75
O
O
CO2Me
Br
OHC
45
(CDCl3, 500 MHz)
0.74
0.72
0.78
2.74
0.97
1.94
1.00
5.12
f1 (ppm)

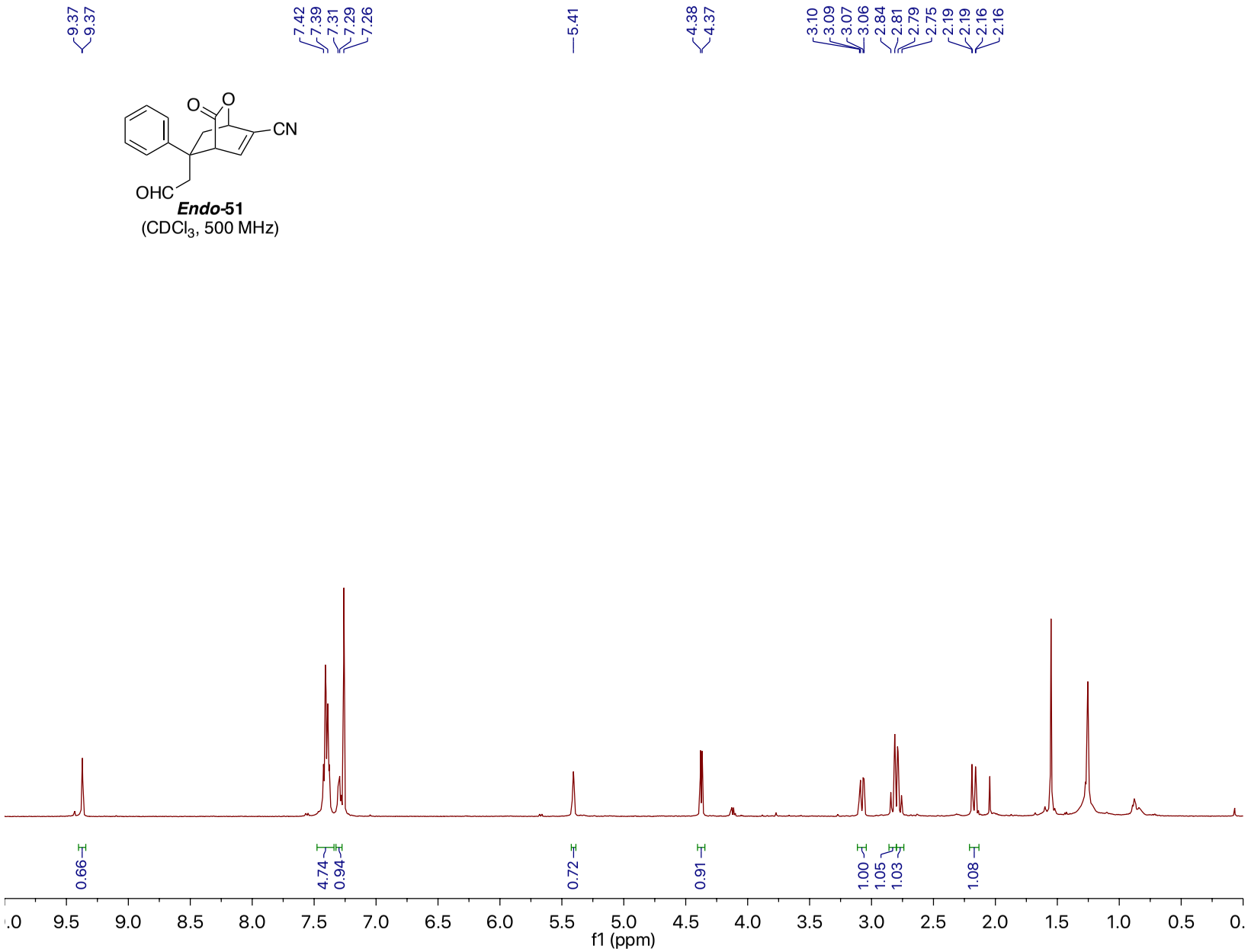

199.75
166.85
161.58
145.19
136.64
77.16
77.09
69.93
55.50
52.85
49.28
35.43
30.24
26.64
O
O
CO2Me
Br
OHC
45
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


9.79
7.75
7.74
7.73
7.64
7.53
7.52
7.26
6.93
6.92
5.61
5.61
5.60
3.03
3.03
3.00
2.58
2.58
2.57
2.51
2.50
2.34
2.32
2.31
2.30
2.04
2.02
1.94
1.92
1.85
1.80
1.80
1.79
O
O
COPh
Br
OHC
46
(CDCl3, 500 MHz)
0.84
1.85
1.00
2.00
0.86
0.87
1.11
1.04
1.13
1.19
5.68
f1 (ppm)

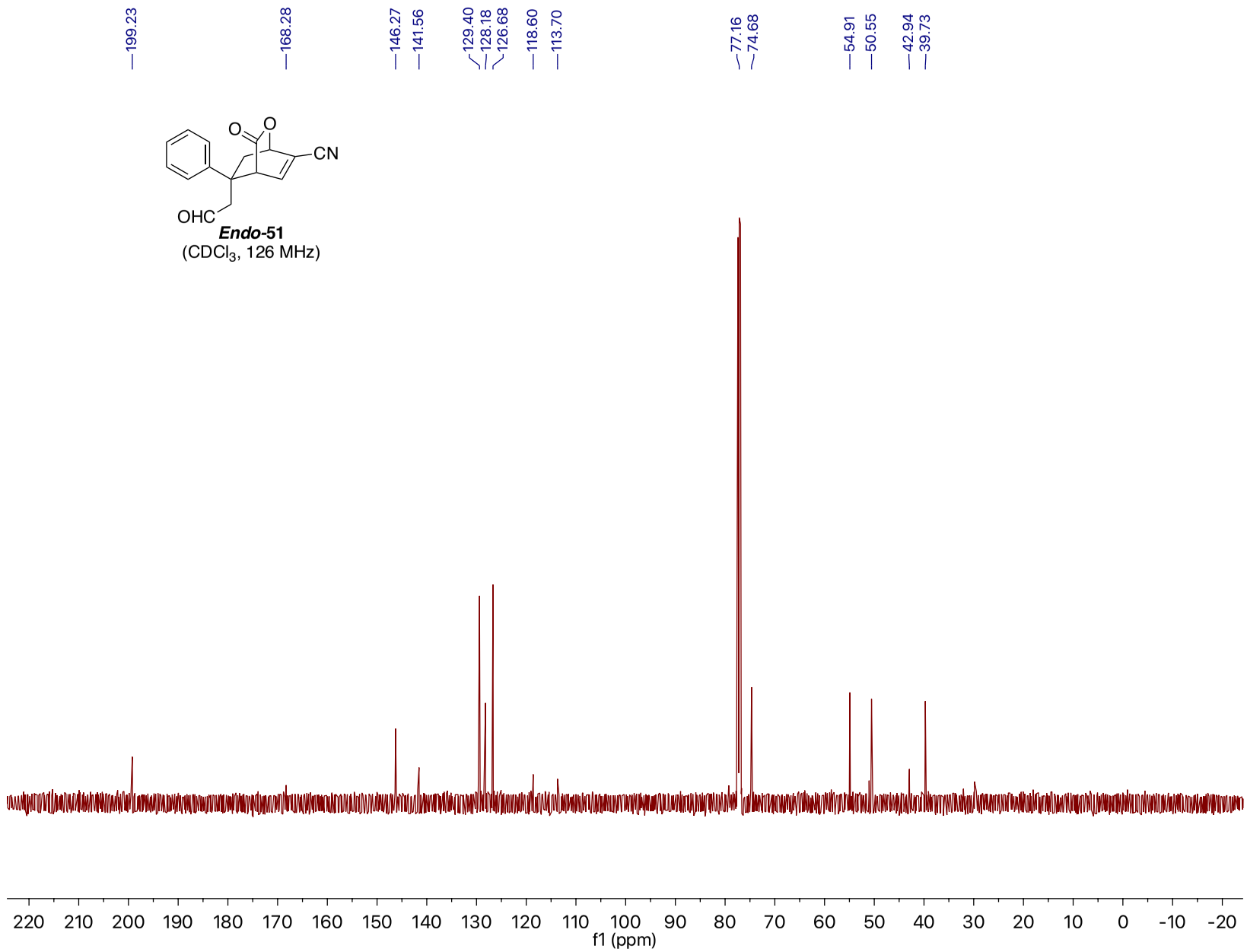

199.61
189.51
167.09
144.78
142.89
135.41
133.84
129.38
129.08
77.93
77.16
70.06
56.22
53.00
49.81
35.63
30.36
26.65
O
O
COPh
Br
OHC
46
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

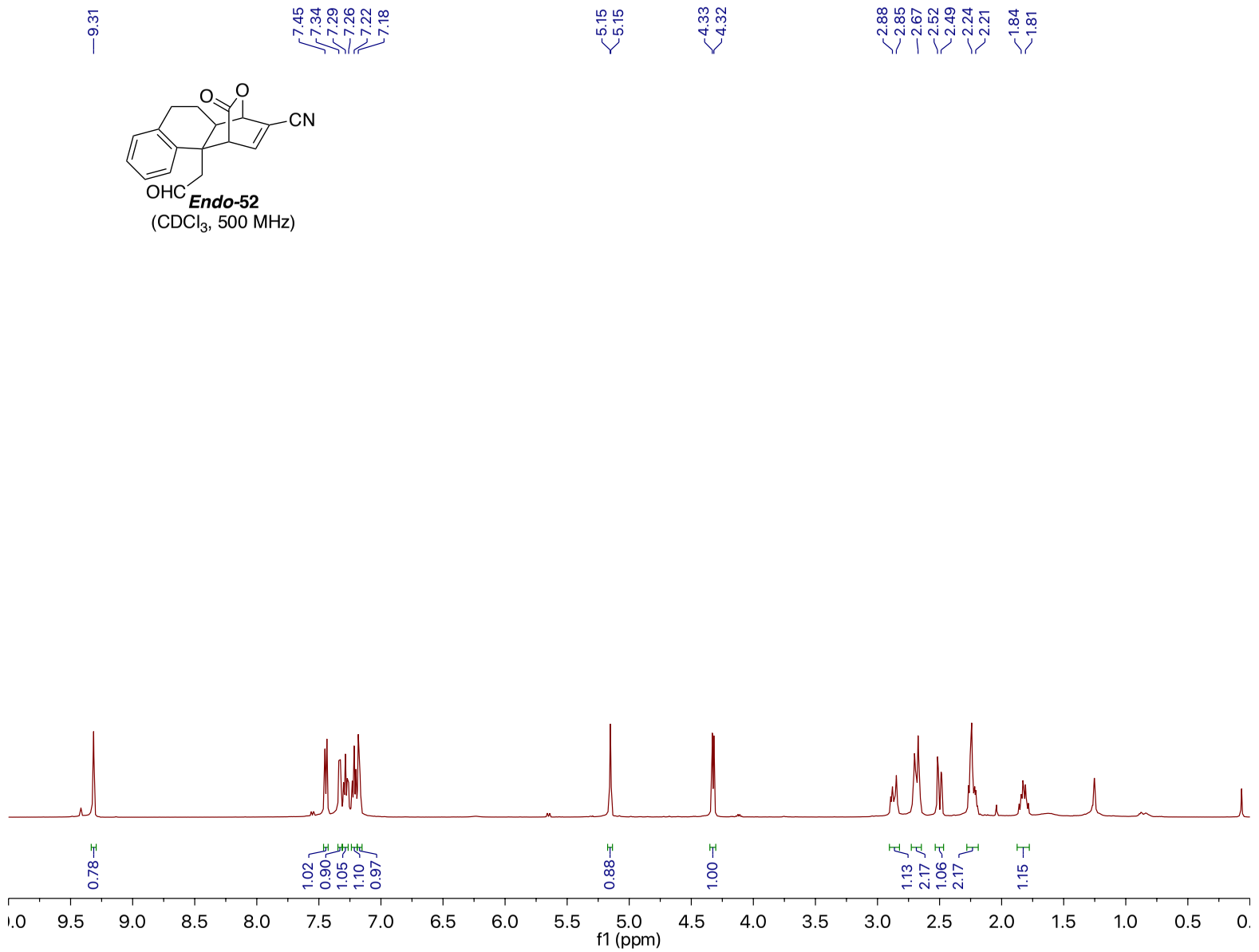

O
O
CO2Me
OHC
47
(CDCl3, 500 MHz)
9.71
7.26
6.73
6.72
6.63
6.62
4.99
4.98
3.88
2.56
2.53
2.40
2.38
2.30
2.17
2.14
2.07
2.01
1.98
1.93
1.90
1.78
1.73
1.69
0.64
1.00
1.25
1.02
1.29
1.36
1.25
1.27
2.74
0.70
0.74
0.76
3.05
f1 (ppm)


200.79
169.48
168.16
132.80
132.18
78.11
77.16
63.43
53.15
51.85
51.30
50.36
36.47
28.51
27.61
O
O
CO2Me
OHC
47
(CDCl3, 126 MHz)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



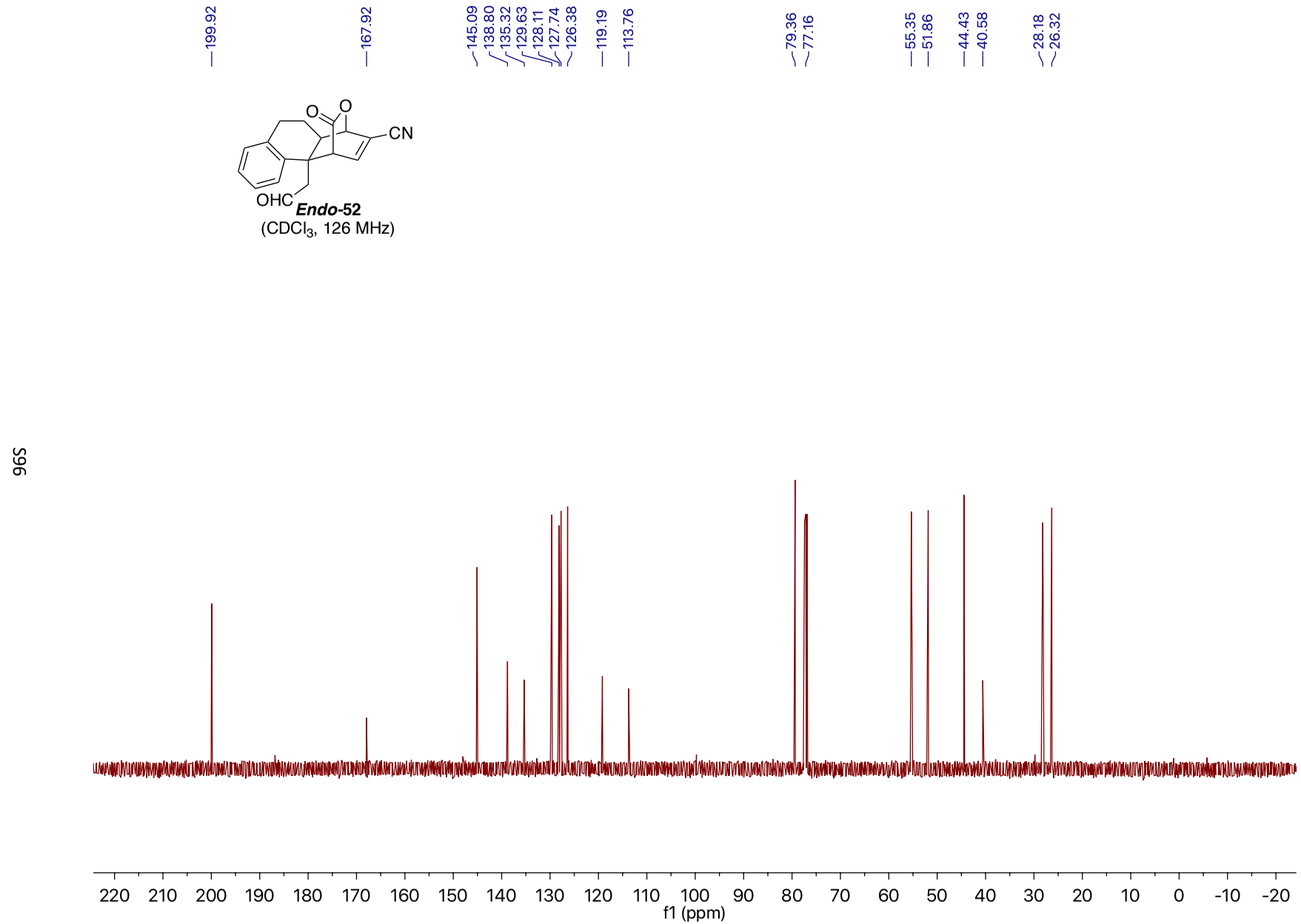
***Endo*-51**
($CDCl_3$, 500 MHz)


199.23
168.28
146.27
141.56
129.40
128.18
126.68
118.60
113.70
77.16
74.68
54.91
50.55
42.94
39.73
O
O
CN
OHC
Endo-51
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

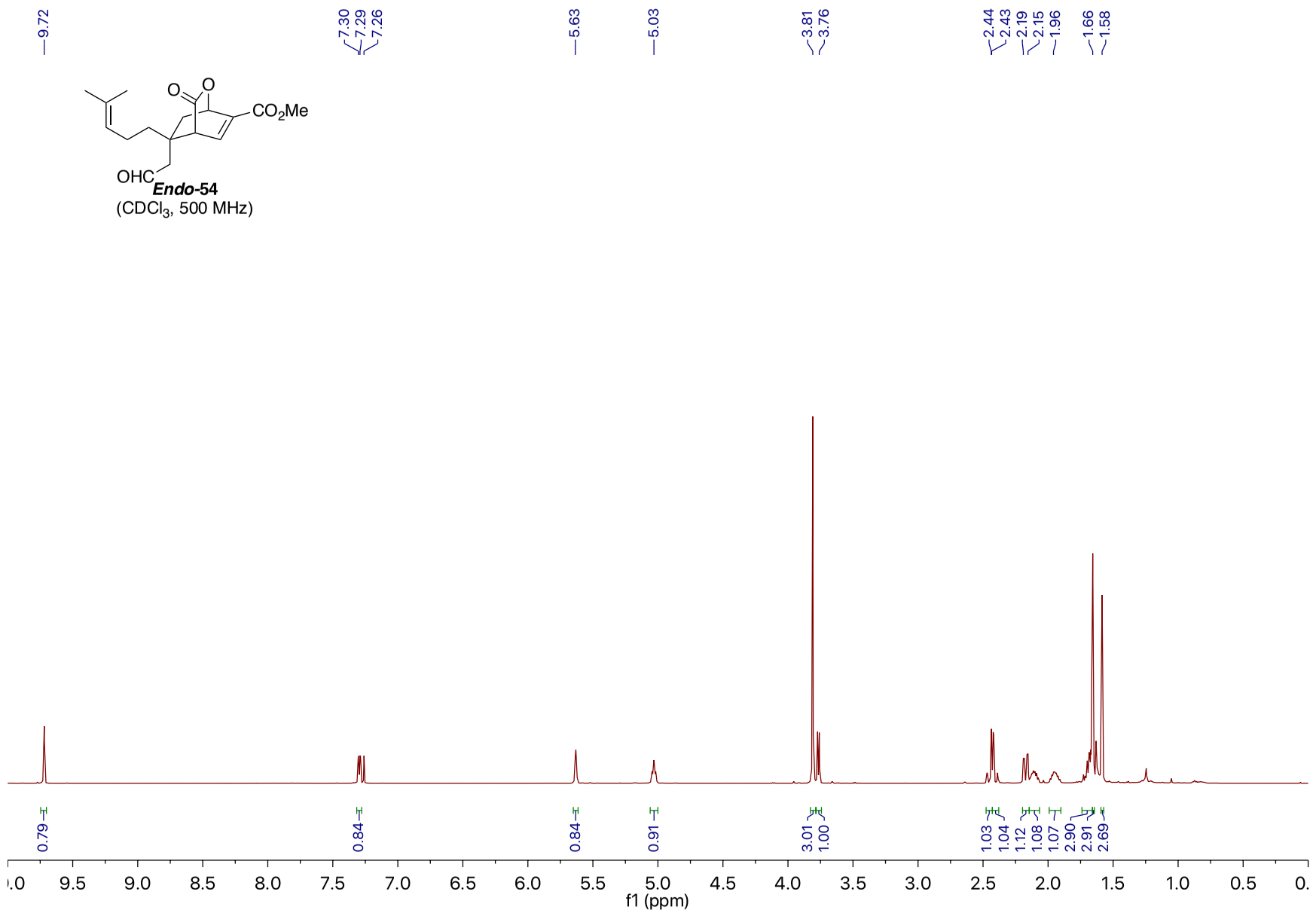


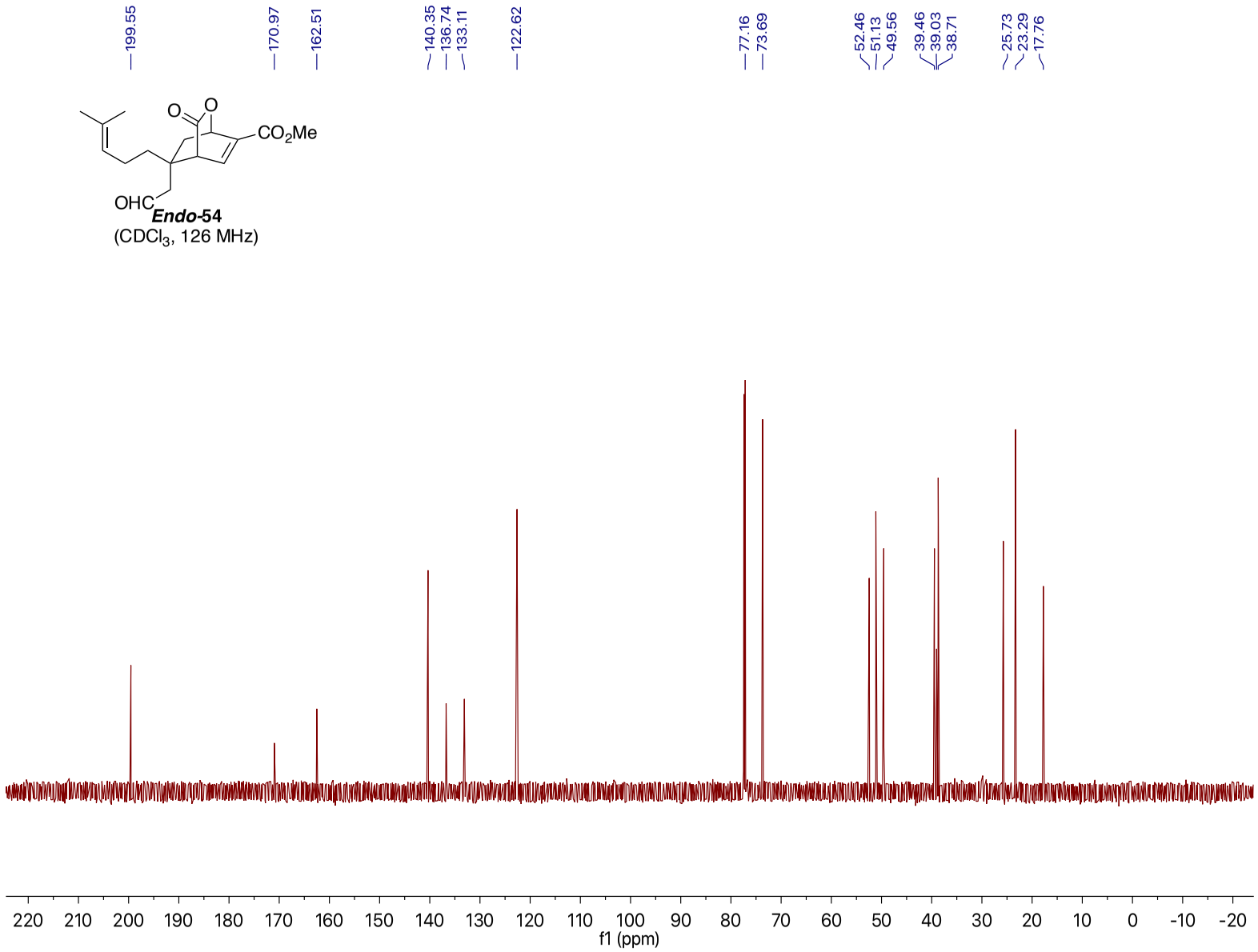
***Endo*-52**

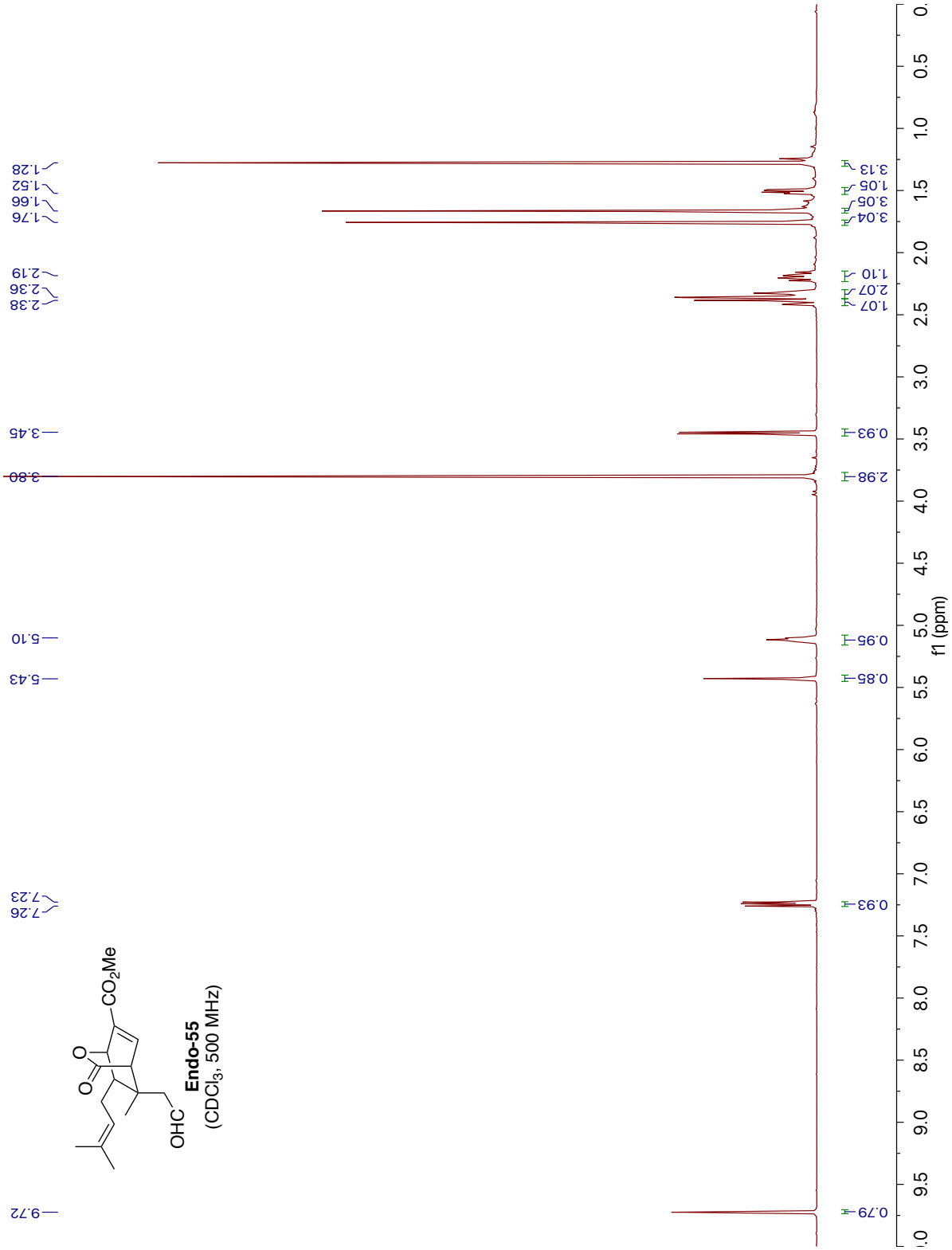
($CDCl_3$, 500 MHz)

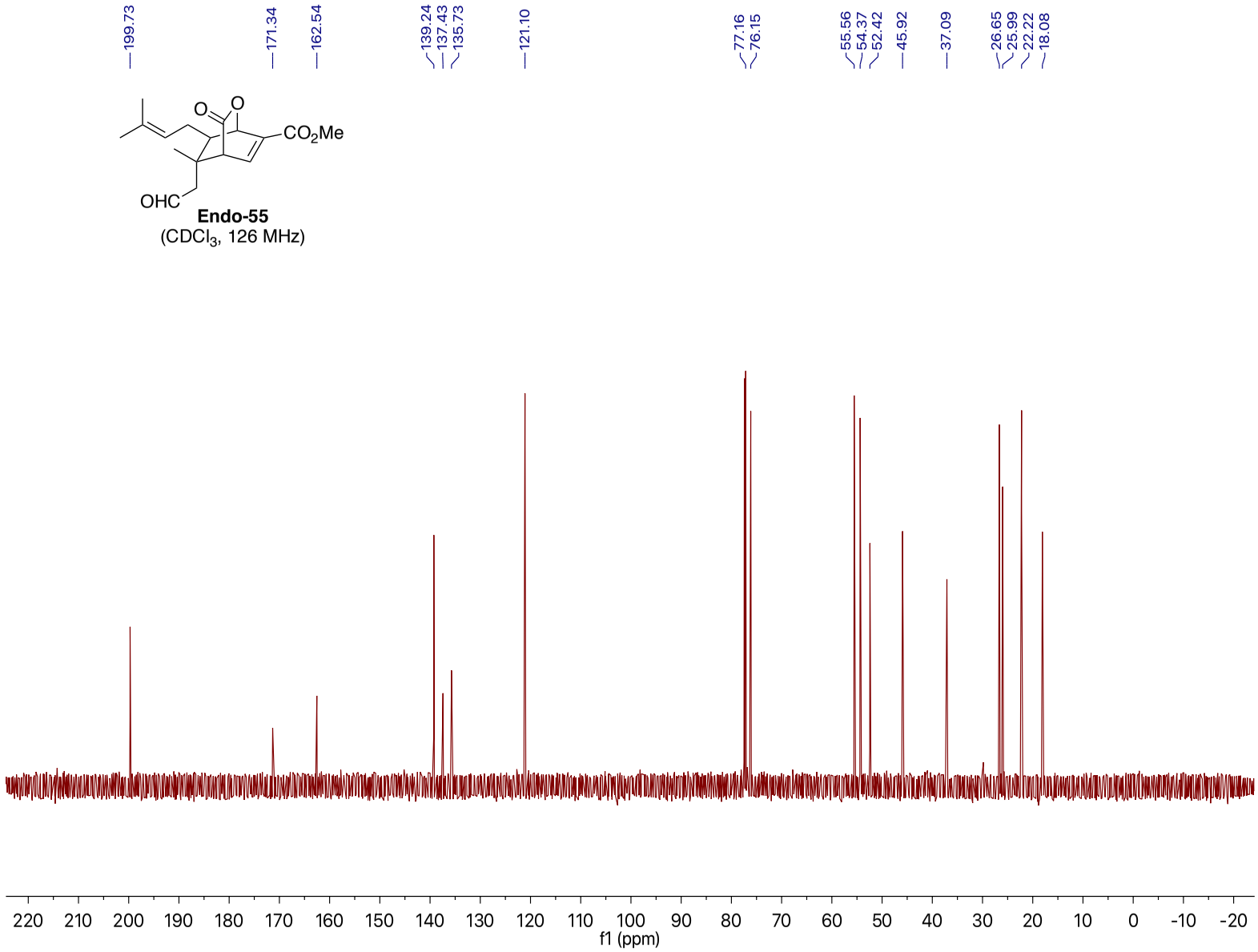


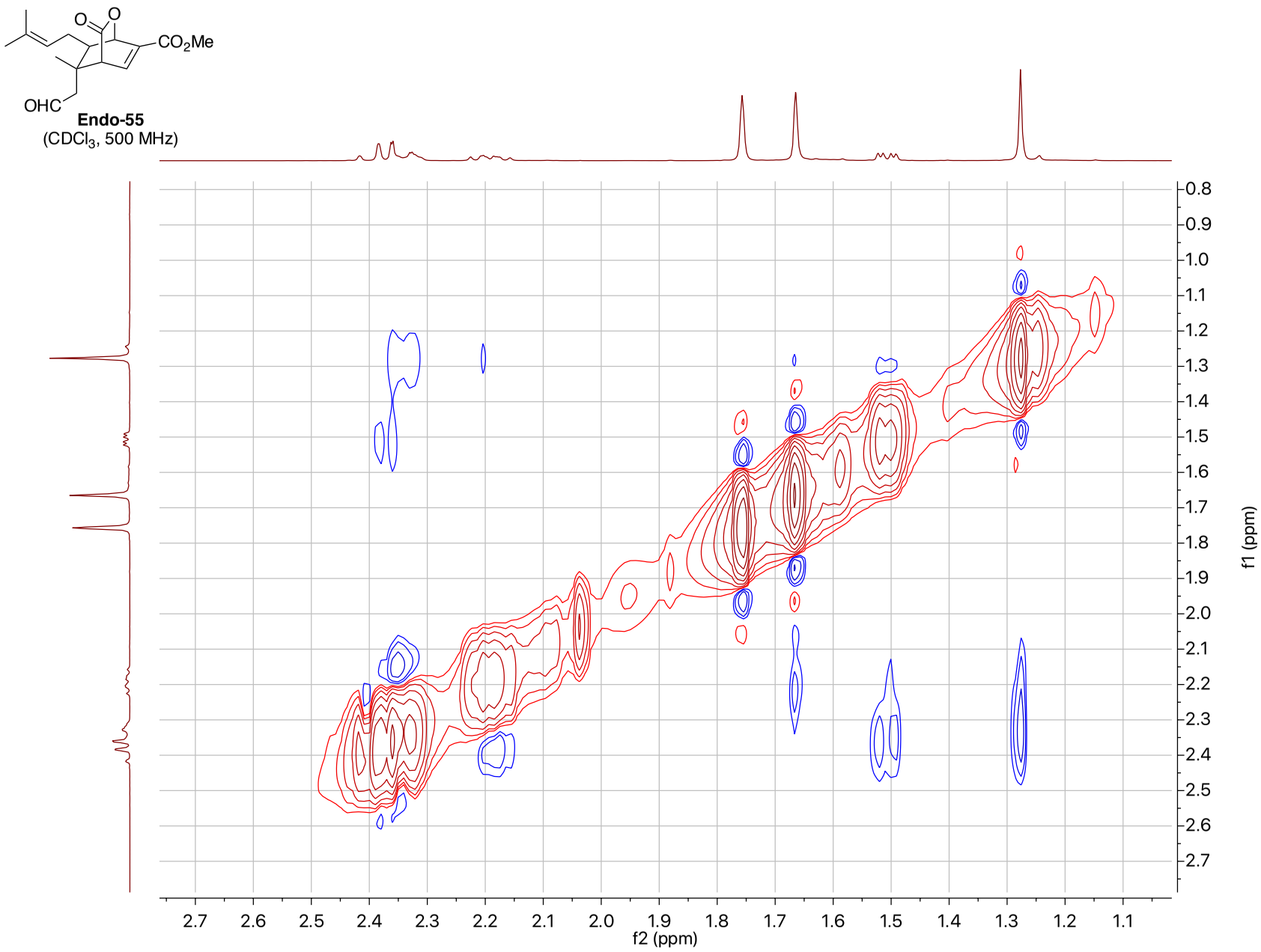
***Endo*-52**
($CDCl_3$, 126 MHz)

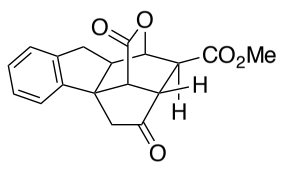

9.72
7.30
7.29
7.26
5.63
5.03
3.81
3.76
2.44
2.43
2.19
2.15
1.96
1.66
1.58
O
O
CO2Me
OHC
Endo-54
(CDCl3, 500 MHz)
0.79
0.84
0.84
0.91
3.01
1.00
1.03
1.04
1.12
1.08
1.07
2.90
2.91
2.69
f1 (ppm)


199.55
170.97
162.51
140.35
136.74
133.11
122.62
77.16
73.69
52.46
51.13
49.56
39.46
39.03
38.71
25.73
23.29
17.76
O
O
CO2Me
OHC
Endo-54
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Endo-55
(CDCl3, 500 MHz)
CO2Me
O
O
OHC
9.72
7.26
7.23
5.43
5.10
3.80
3.45
2.38
2.36
2.19
1.76
1.66
1.52
1.28
0.79
0.93
0.85
0.95
2.98
0.93
1.07
2.07
1.10
3.04
3.05
1.05
3.13
f1 (ppm)

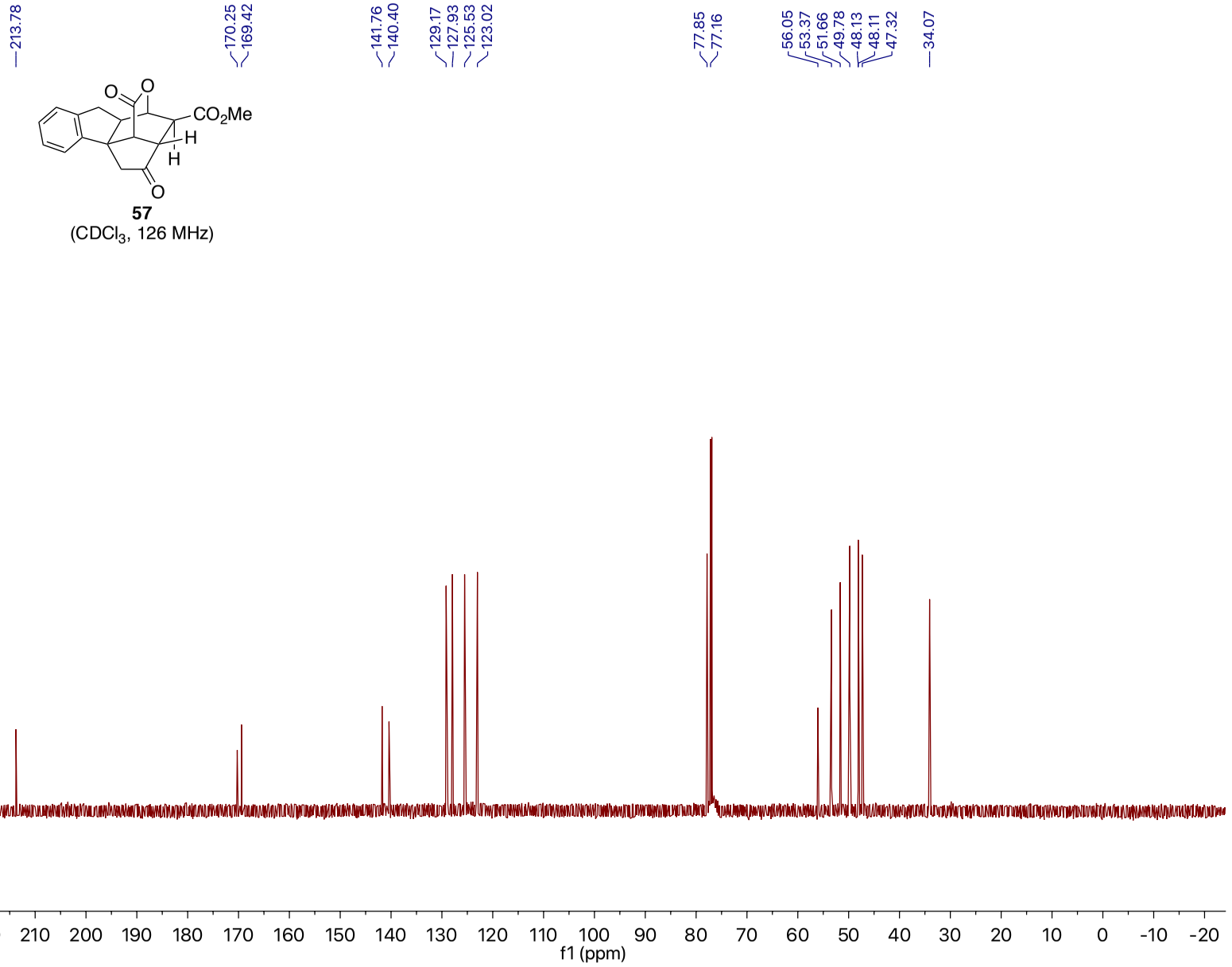

199.73
171.34
162.54
139.24
137.43
135.73
121.10
77.16
76.15
55.56
54.37
52.42
45.92
37.09
26.65
25.99
22.22
18.08
O
O
CO2Me
OHC
Endo-55
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

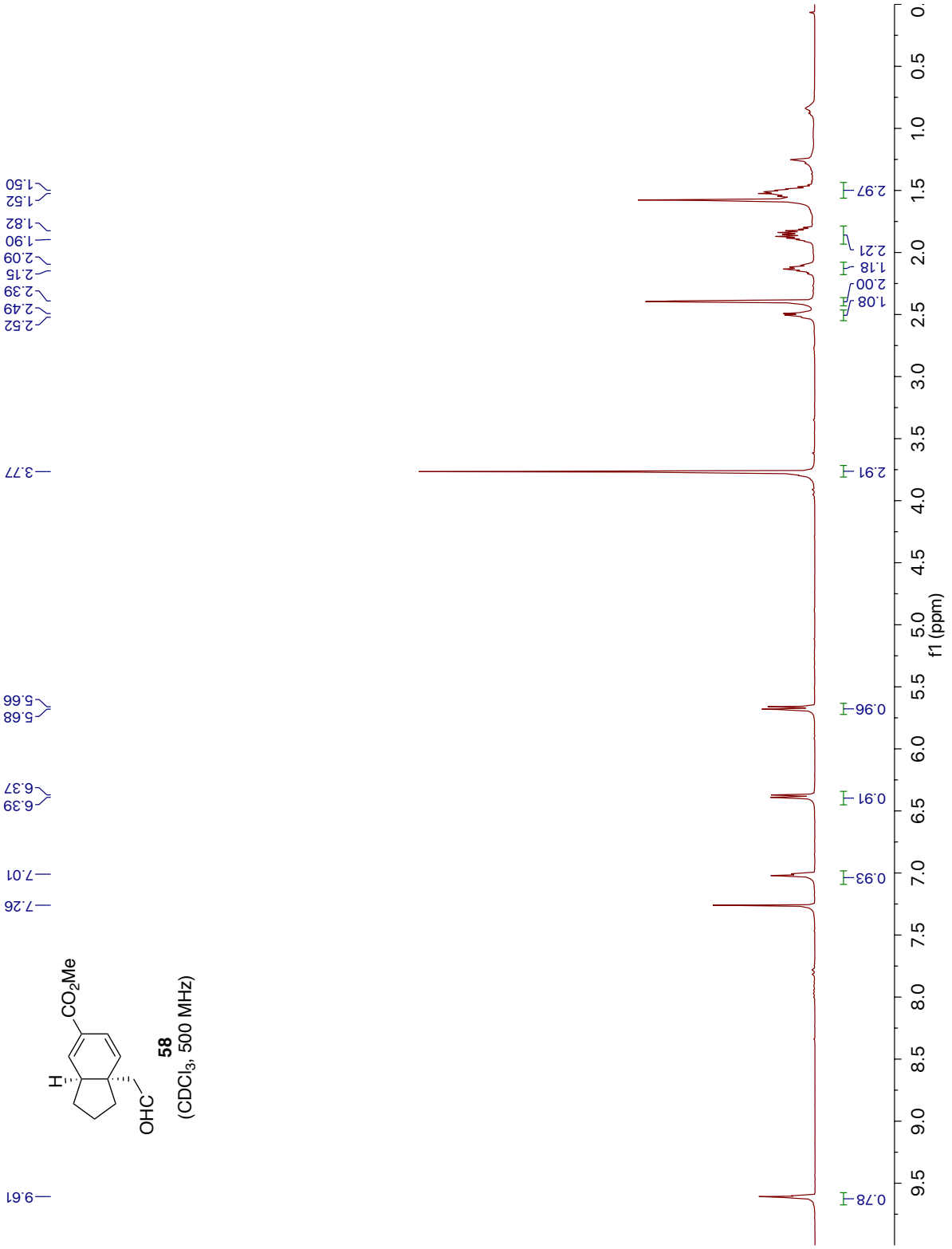

O
O
CO2Me
OHC
Endo-55
(CDCl3, 500 MHz)
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
f1 (ppm)
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
f2 (ppm)

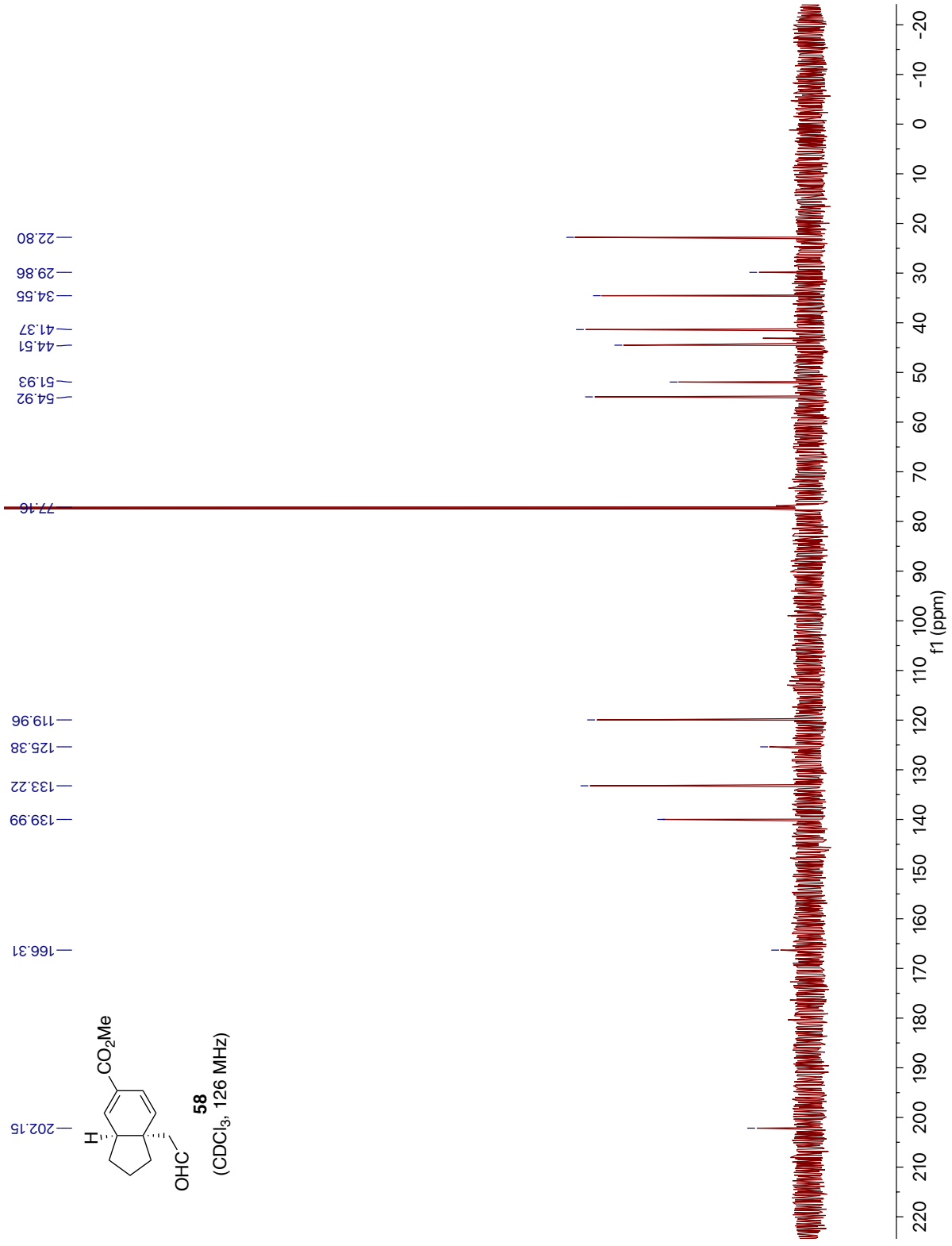


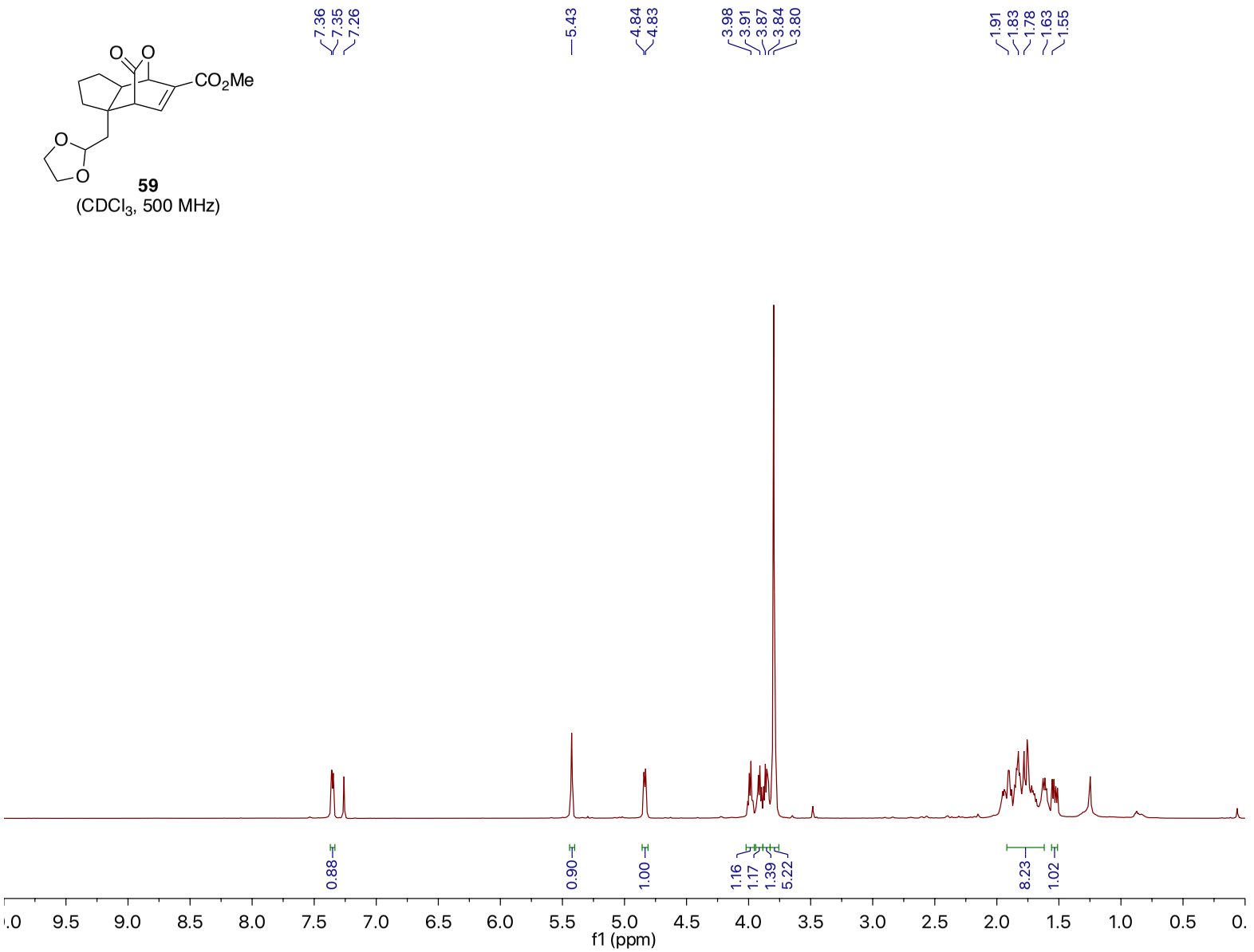
57

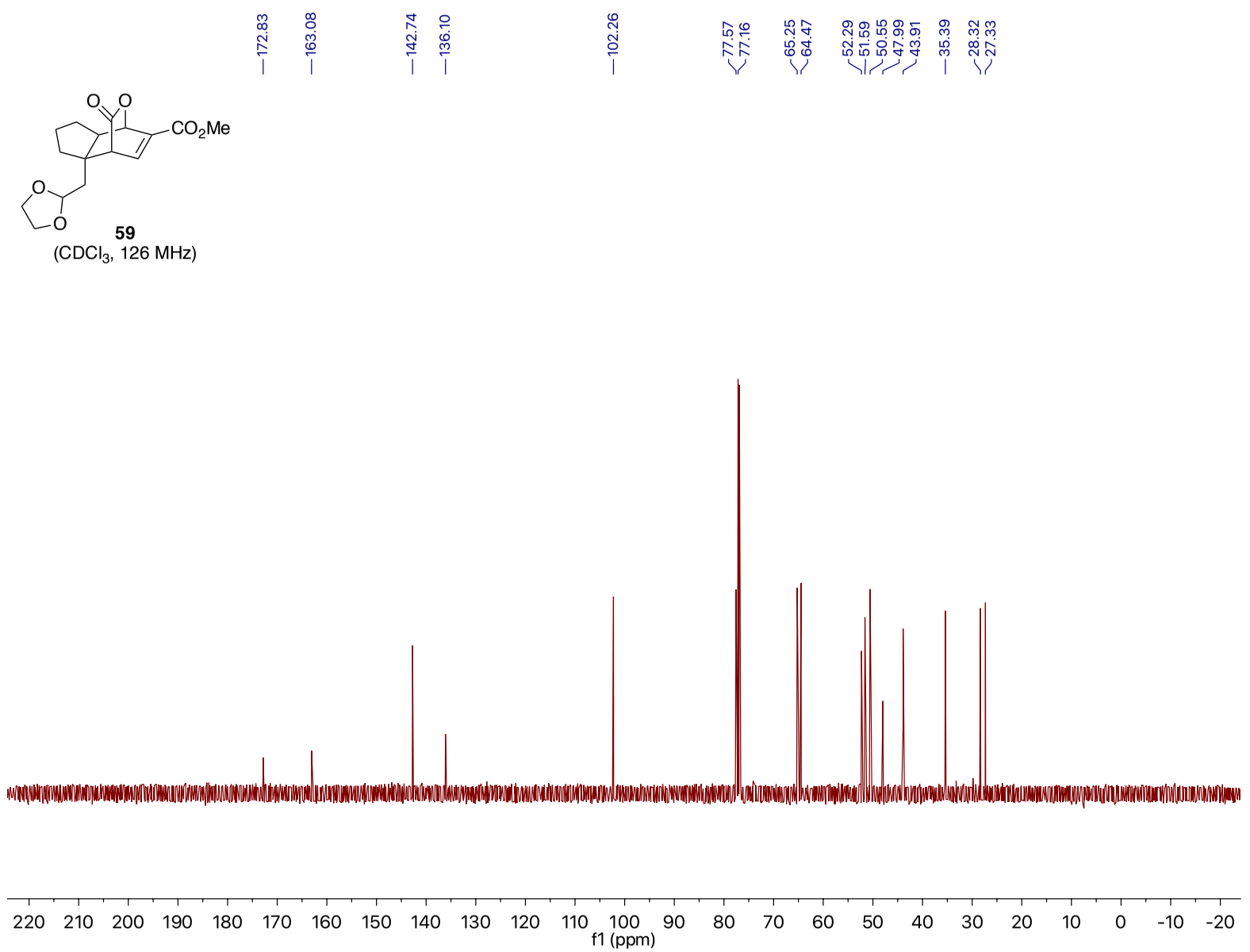
($CDCl_3$, 500 MHz)

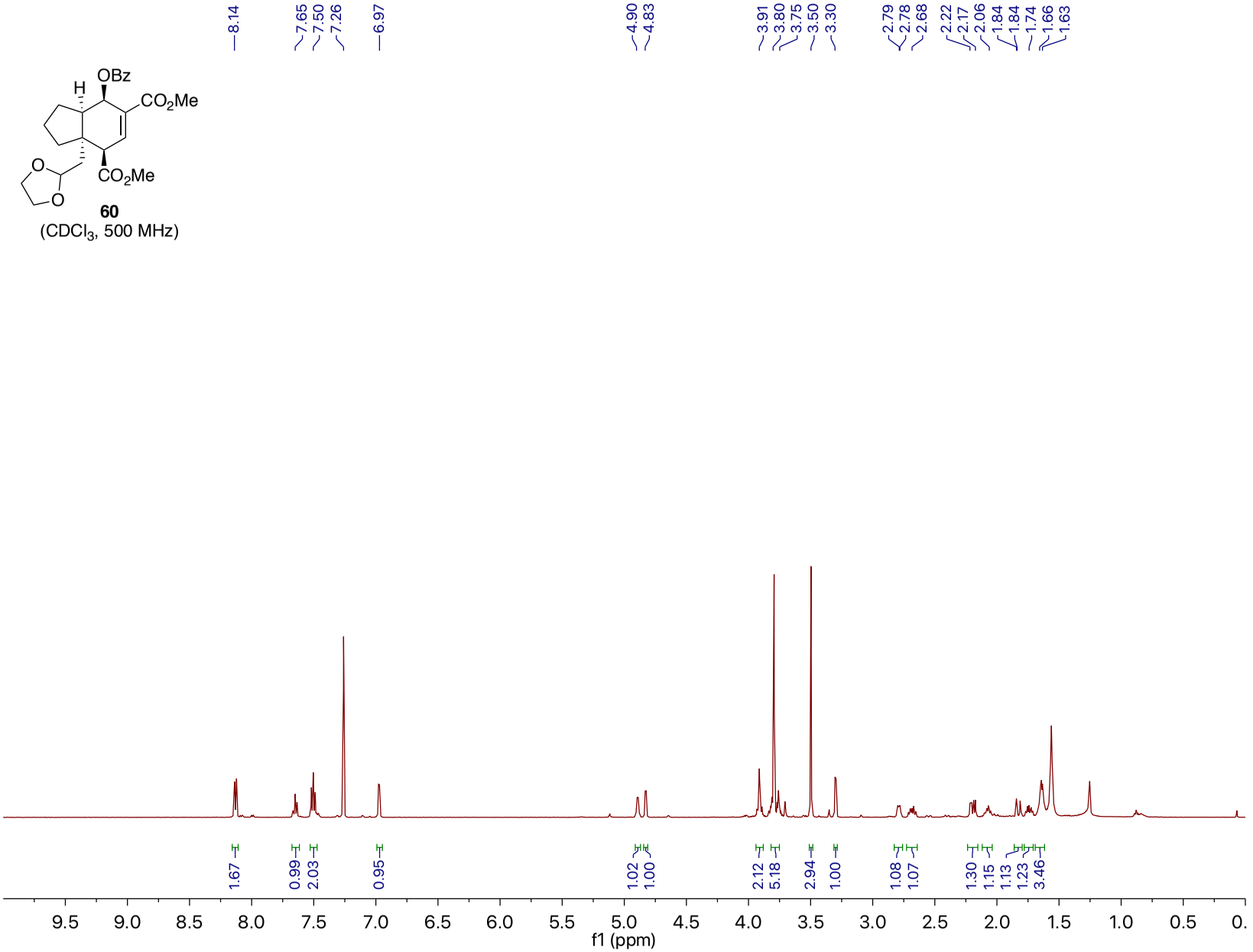

213.78
170.25
169.42
141.76
140.40
129.17
127.93
125.53
123.02
77.85
77.16
56.05
53.37
51.66
49.78
48.13
48.11
47.32
34.07
O
O
CO2Me
H
H
O
57
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

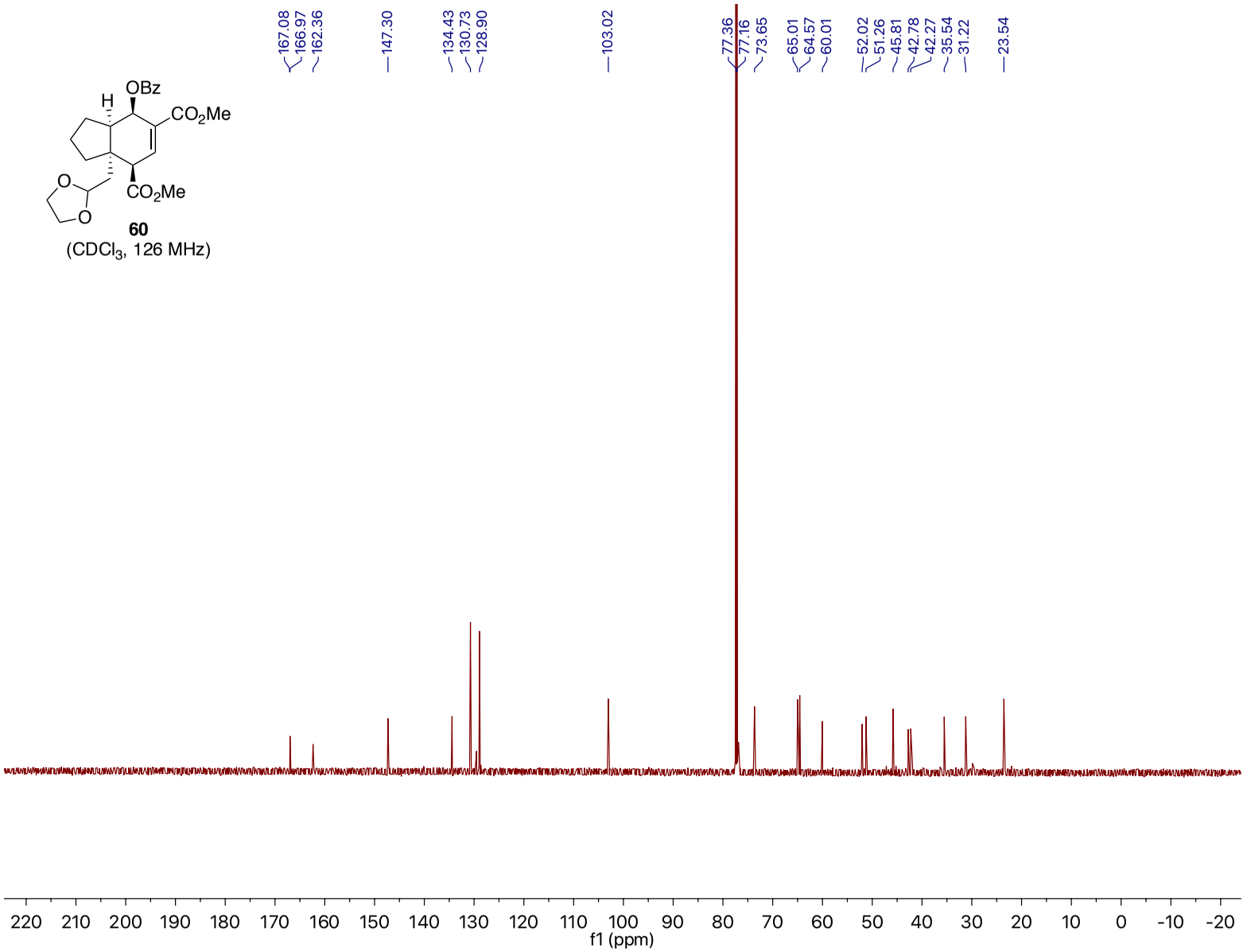

9.61
7.26
7.01
6.39
6.37
5.68
5.66
3.77
2.52
2.49
2.39
2.15
2.09
1.90
1.82
1.52
1.50
0.78
2.97
2.21
1.18
2.00
1.08
2.91
0.96
0.91
0.93
f1 (ppm)
CO2Me
H
OHC
58
(CDCl3, 500 MHz)

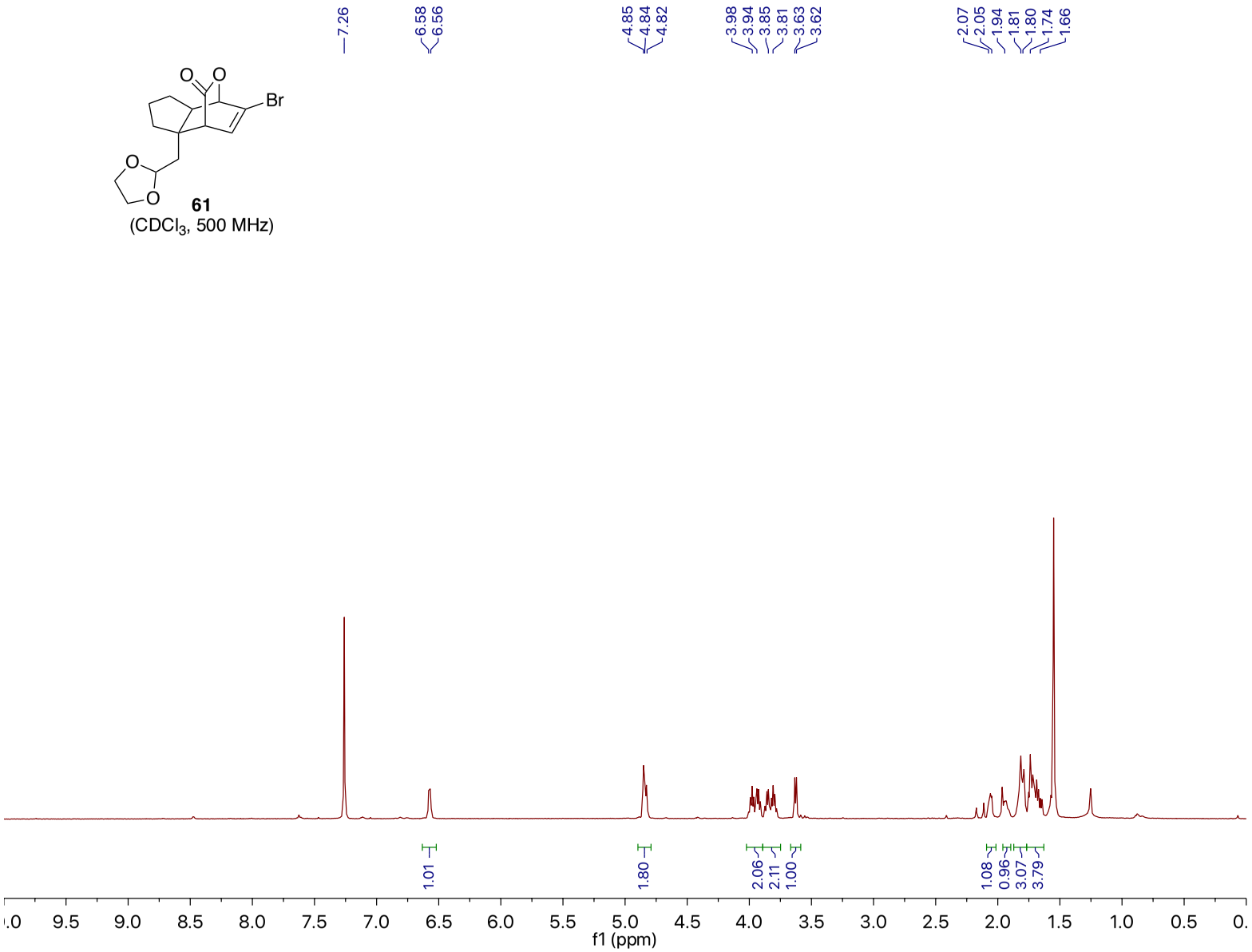

22.80
29.86
34.55
41.37
44.51
51.93
54.92
77.16
119.96
125.38
133.22
139.99
166.31
202.15
H
CO2Me
OHC
58
(CDCl3, 126 MHz)
f1 (ppm)

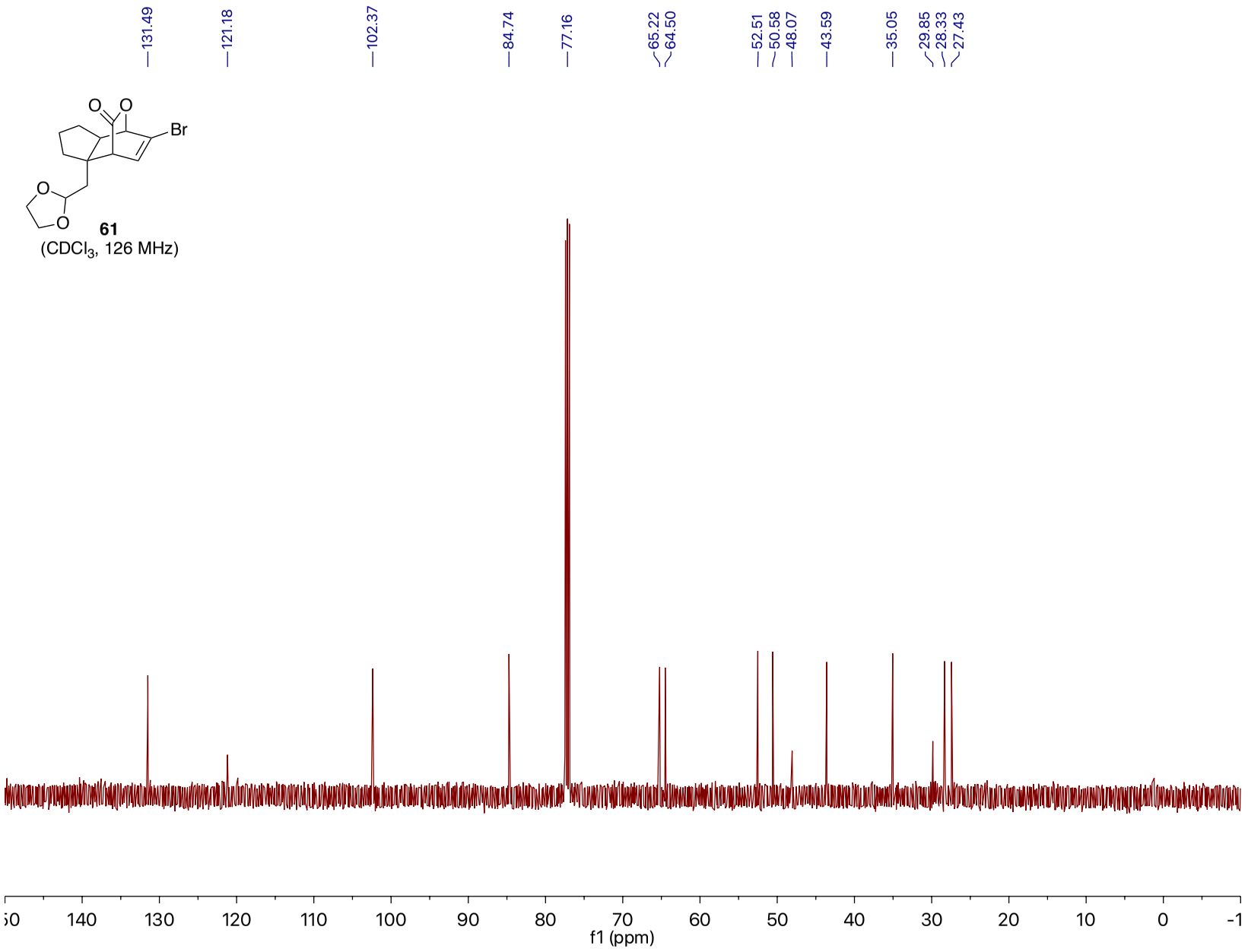

7.36
7.35
7.26
5.43
4.84
4.83
3.98
3.91
3.87
3.84
3.80
1.91
1.83
1.78
1.63
1.55
O
O
CO2Me
O
O
59
(CDCl3, 500 MHz)
0.88
0.90
1.00
1.16
1.17
1.39
5.22
8.23
1.02
f1 (ppm)


172.83
163.08
142.74
136.10
102.26
77.57
77.16
65.25
64.47
52.29
51.59
50.55
47.99
43.91
35.39
28.32
27.33
O
O
CO2Me
O
O
59
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.14
7.65
7.50
7.26
6.97
4.90
4.83
3.91
3.80
3.75
3.50
3.30
2.79
2.78
2.68
2.22
2.17
2.06
1.84
1.84
1.74
1.66
1.63
OBz
H
CO2Me
CO2Me
O
O
60
(CDCl3, 500 MHz)
1.67
0.99
2.03
0.95
1.02
1.00
2.12
5.18
2.94
1.00
1.08
1.07
1.30
1.15
1.13
1.23
3.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

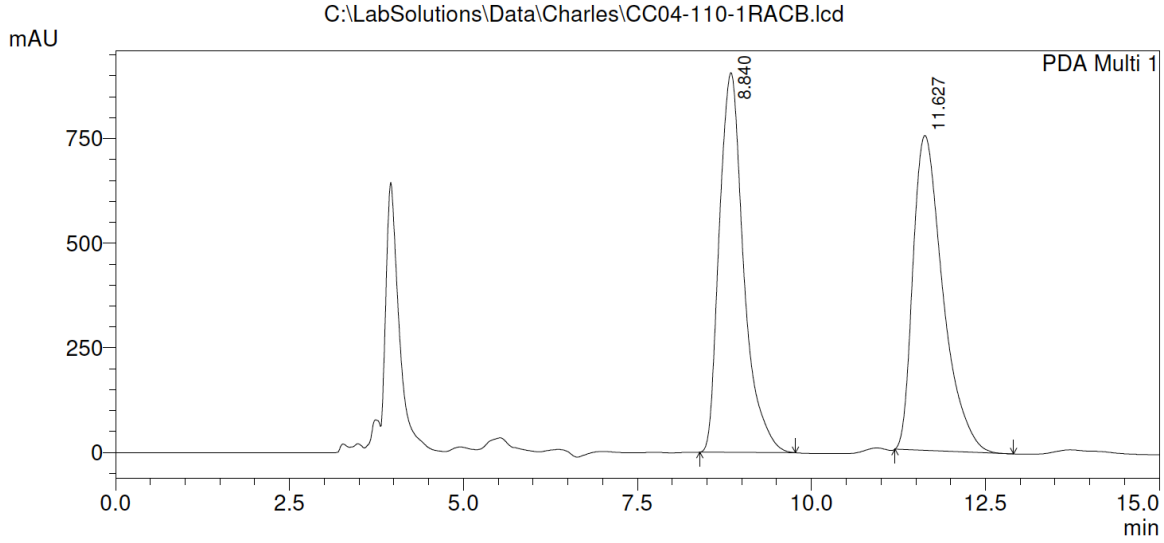

167.08
166.97
162.36
147.30
134.43
130.73
128.90
103.02
77.36
77.16
73.65
65.01
64.57
60.01
52.02
51.26
45.81
42.78
42.27
35.54
31.22
23.54
OBz
H
CO2Me
CO2Me
O
O
O
60
(CDCl3, 126 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.26
6.58
6.56
4.85
4.84
4.82
3.98
3.94
3.85
3.81
3.63
3.62
2.07
2.05
1.94
1.81
1.80
1.74
1.66
O
O
Br
O
O
61
(CDCl3, 500 MHz)
1.01
1.80
2.06
2.11
1.00
1.08
0.96
3.07
3.79
f1 (ppm)


131.49
121.18
102.37
84.74
77.16
65.22
64.50
52.51
50.58
48.07
43.59
35.05
29.85
28.33
27.43
O
O
Br
O
O
61
(CDCl3, 126 MHz)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

I. HPLC Traces *(Note: All traces are of the corresponding Wittig products)*

Racemic ***Endo*-24** (Chiralpak IA, Hexanes/*i*PrOH 85:15, 215 nm)

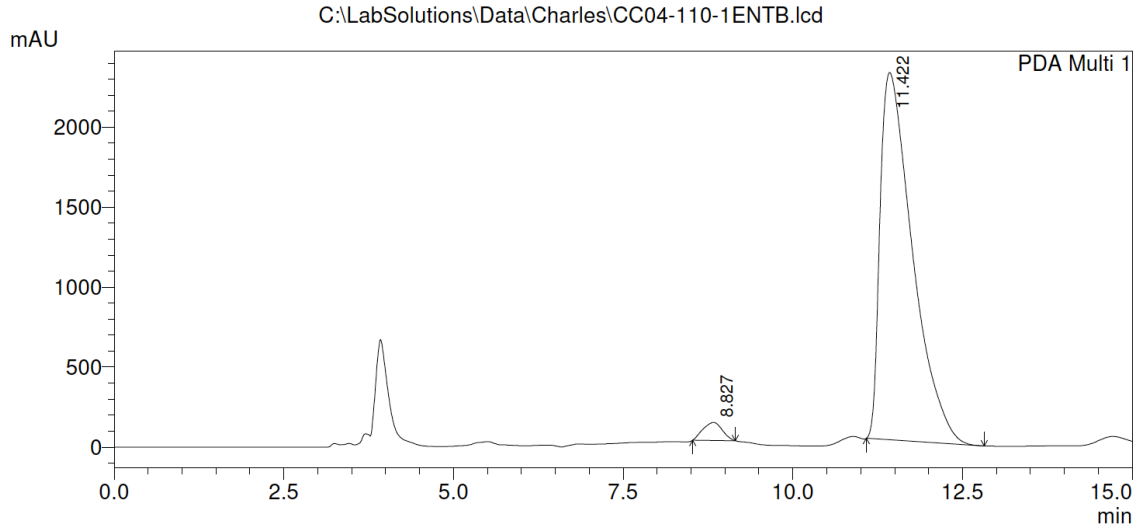


PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.840	22126644	907466	49.559	54.668
2	11.627	22519980	752489	50.441	45.332
Total		44646624	1659956	100.000	100.000

Enantioenriched ***Endo*-24** (Chiralpak IA, Hexanes/*i*PrOH 85:15, 215 nm)

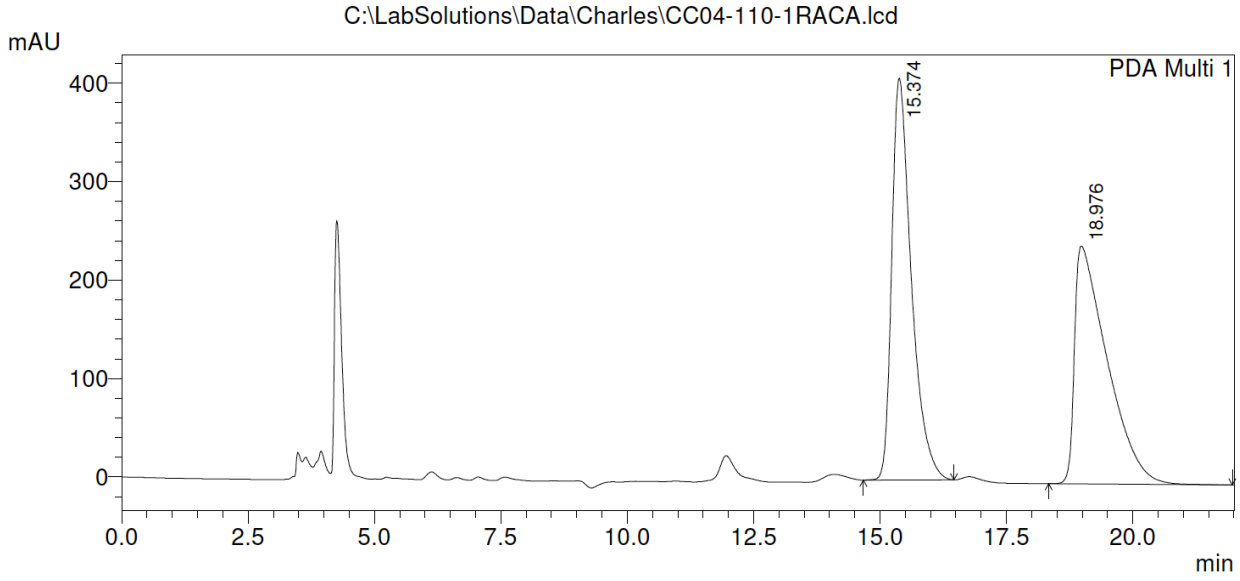


PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.827	2233008	112841	2.841	4.682
2	11.422	76354430	2297192	97.159	95.318
Total		78587438	2410033	100.000	100.000

Racemic ***Exo*-24** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 215 nm)

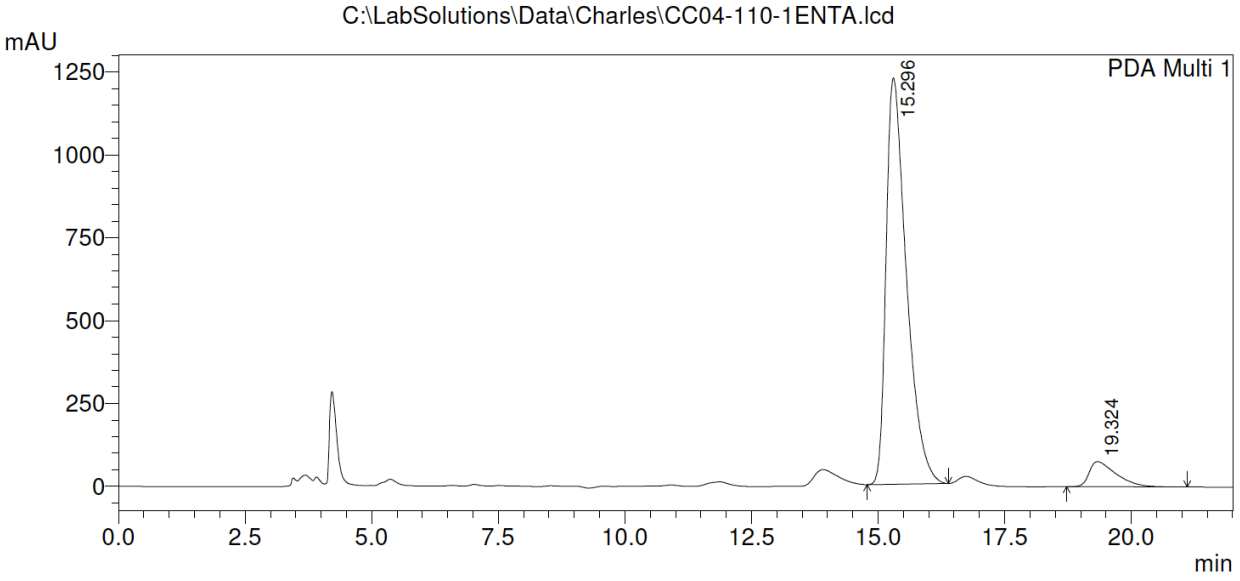


PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.374	11016577	407996	50.358	62.802
2	18.976	10859945	241660	49.642	37.198
Total		21876522	649656	100.000	100.000

Enantioenriched ***Exo*-24** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 215 nm)

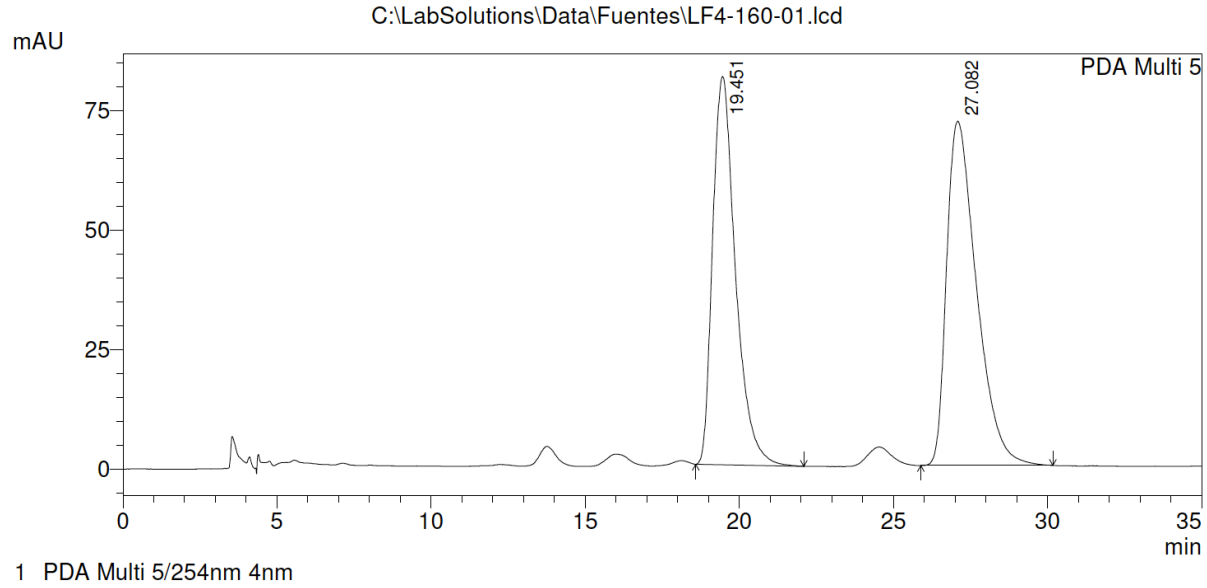


PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.296	34284306	1225572	92.408	94.159
2	19.324	2816847	76021	7.592	5.841
Total		37101153	1301592	100.000	100.000

Racemic ***Endo*-28** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)



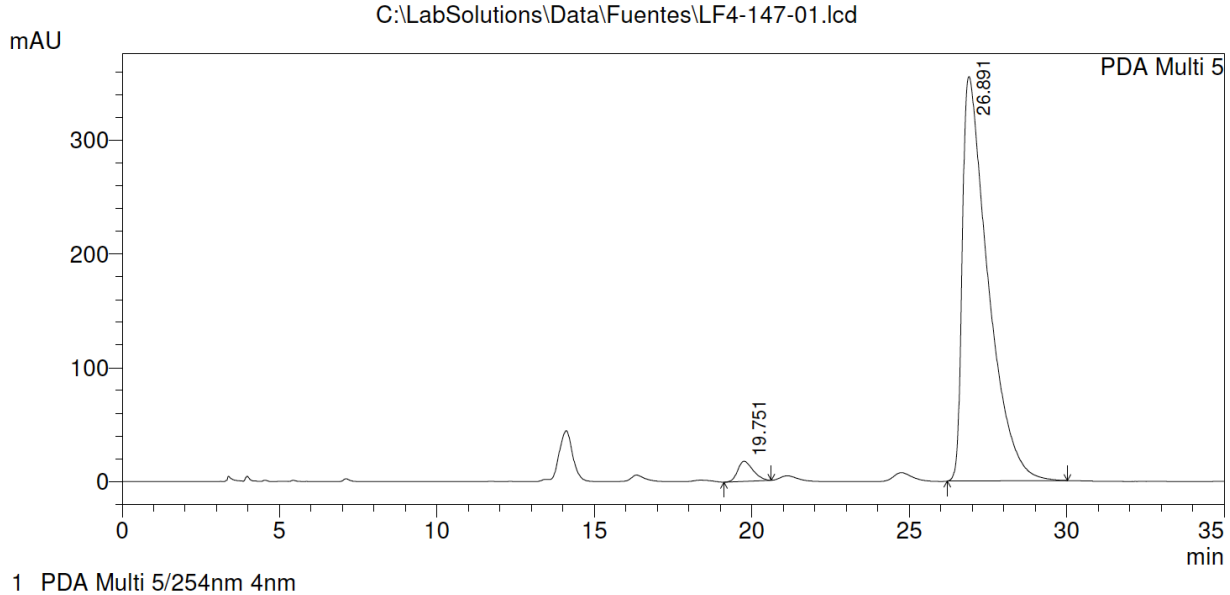
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.451	4186247	81240	46.243	52.996
2	27.082	4866430	72055	53.757	47.004
Total		9052677	153295	100.000	100.000

Enantioenriched ***Endo*-28** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)



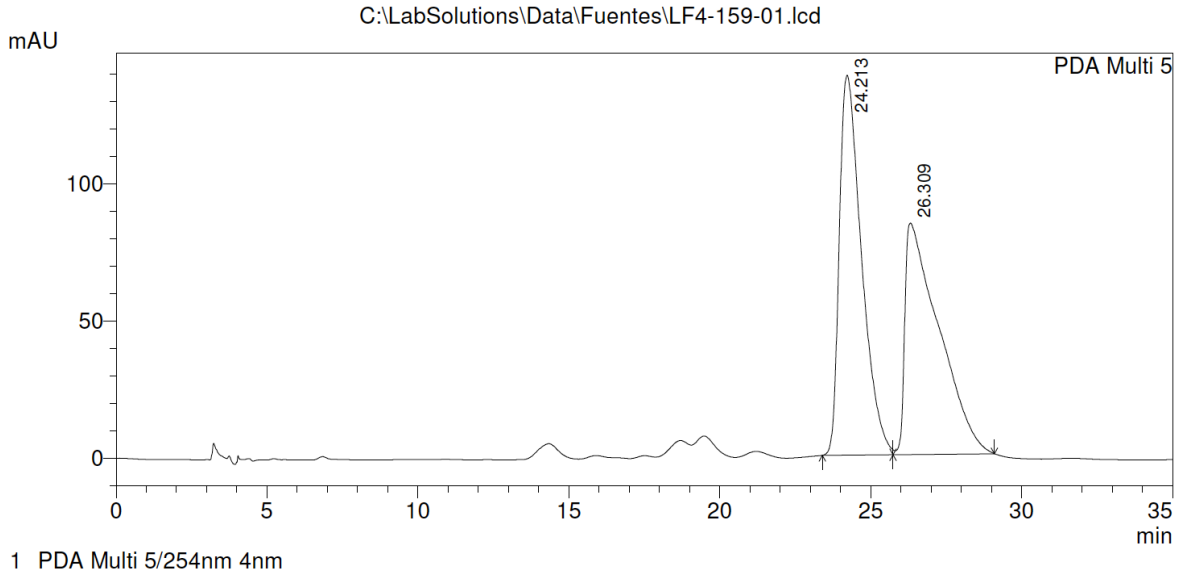
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.751	596314	17664	2.879	4.735
2	26.891	20116790	355351	97.121	95.265
Total		20713105	373014	100.000	100.000

Racemic ***Exo*-28** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)



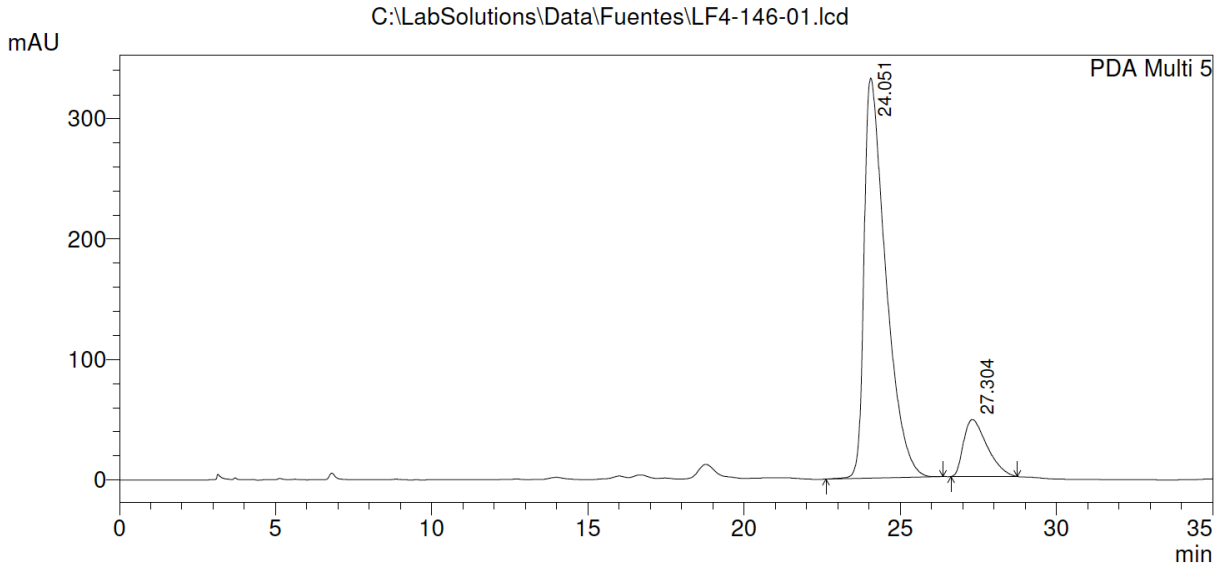
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.213	7093311	138542	51.733	62.132
2	26.309	6618194	84440	48.267	37.868
Total		13711505	222982	100.000	100.000

Enantioenriched ***Exo*-28** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)



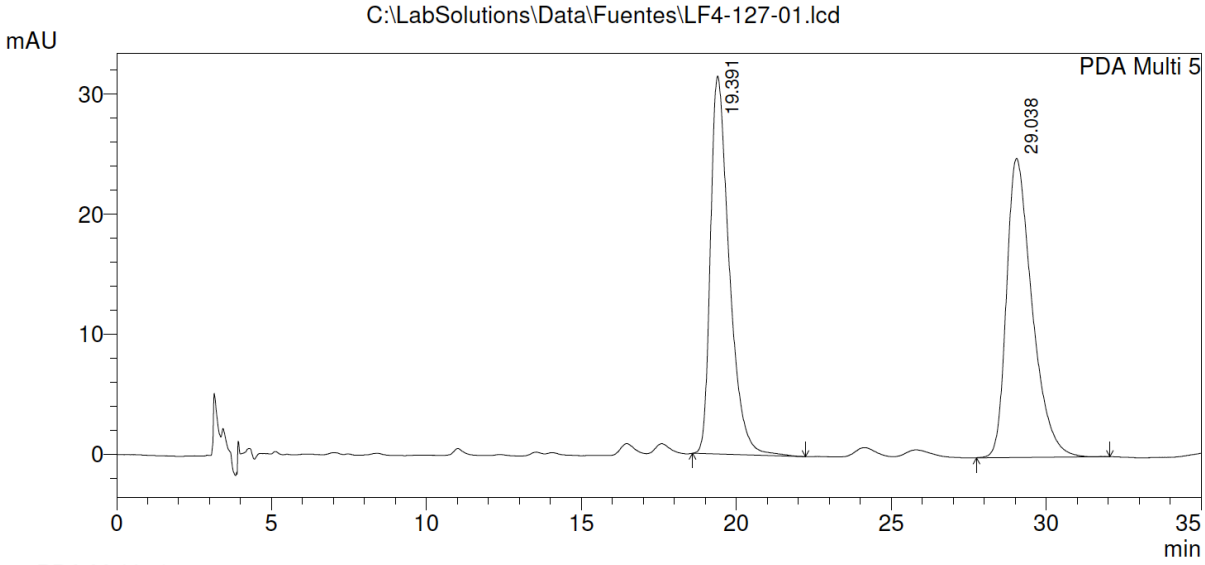
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.051	16033603	332290	86.572	87.527
2	27.304	2486878	47354	13.428	12.473
Total		18520481	379644	100.000	100.000

Racemic ***Endo*-29** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)



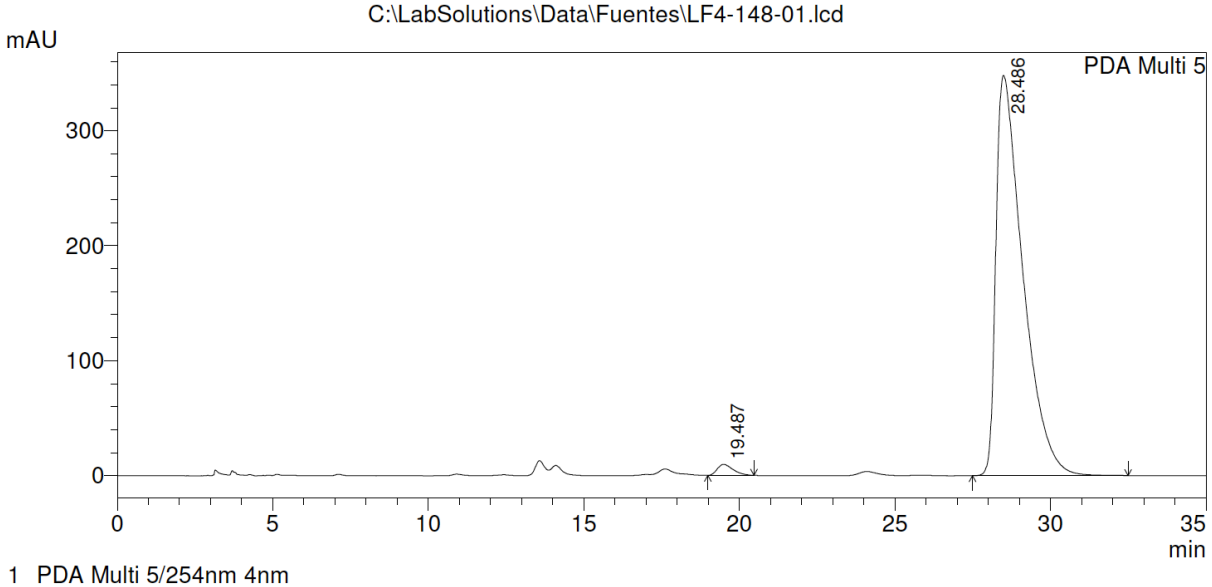
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.391	1326560	31475	48.151	55.827
2	29.038	1428418	24904	51.849	44.173
Total		2754978	56379	100.000	100.000

Enantioenriched ***Endo*-29** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)



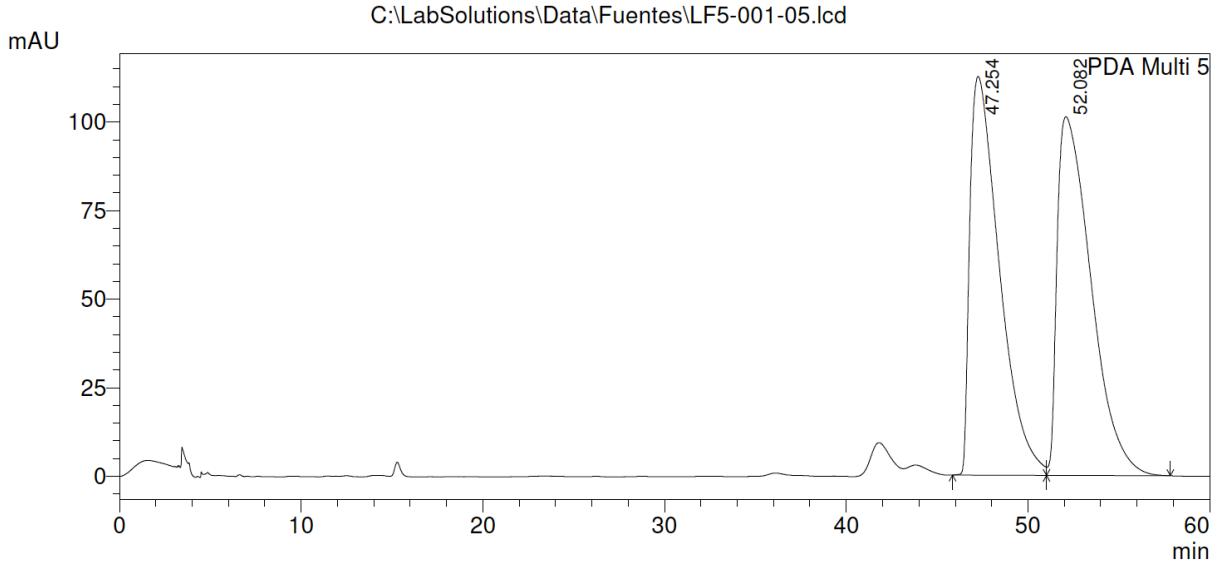
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.487	339093	9531	1.595	2.664
2	28.486	20918263	348244	98.405	97.336
Total		21257356	357776	100.000	100.000

Racemic ***Endo*-30** (Chiralpak AD-H, Hexanes/*i*PrOH 98:2, 254 nm)



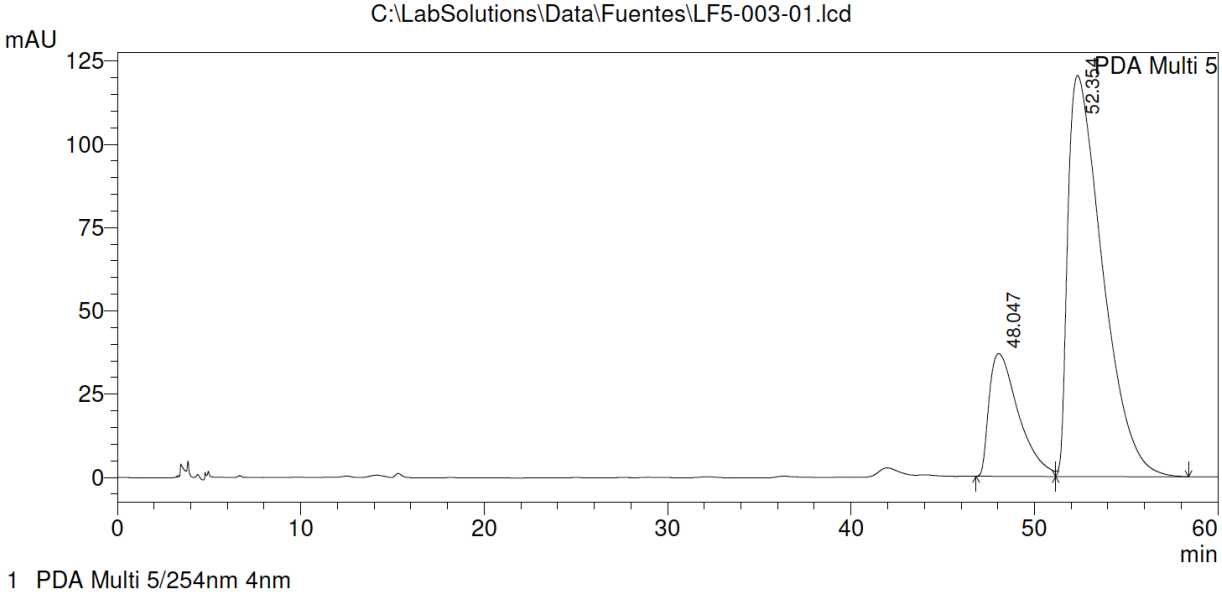
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.254	12710315	112585	49.179	52.636
2	52.082	13134708	101309	50.821	47.364
Total		25845024	213894	100.000	100.000

Enantioenriched ***Endo*-30** (Chiralpak AD-H, Hexanes/*i*PrOH 98:2, 254 nm)



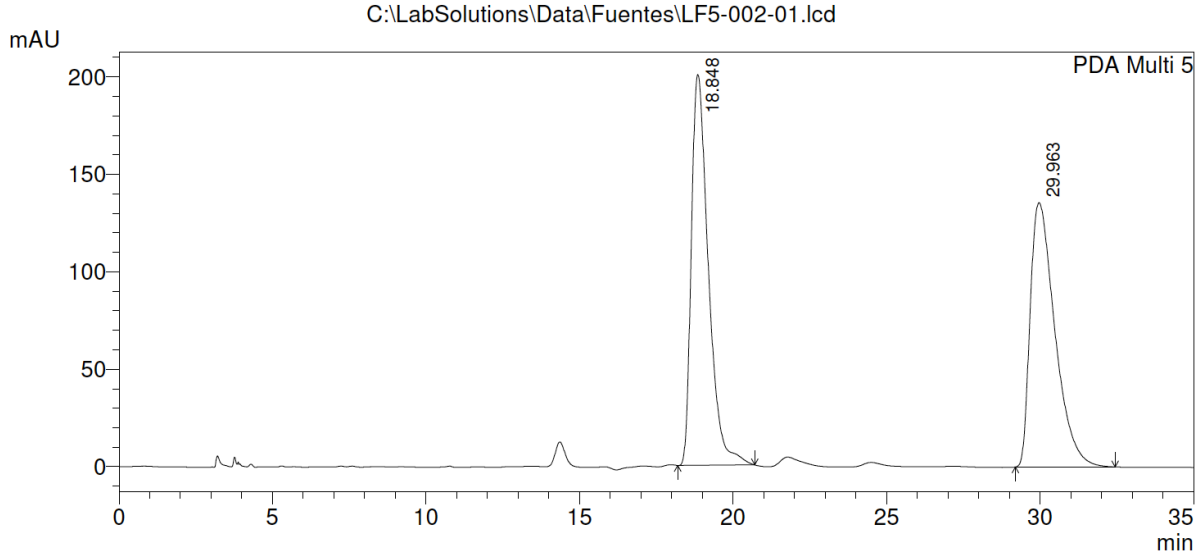
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.047	4095815	36791	20.600	23.414
2	52.354	15786664	120341	79.400	76.586
Total		19882479	157132	100.000	100.000

Racemic ***Exo*-30** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



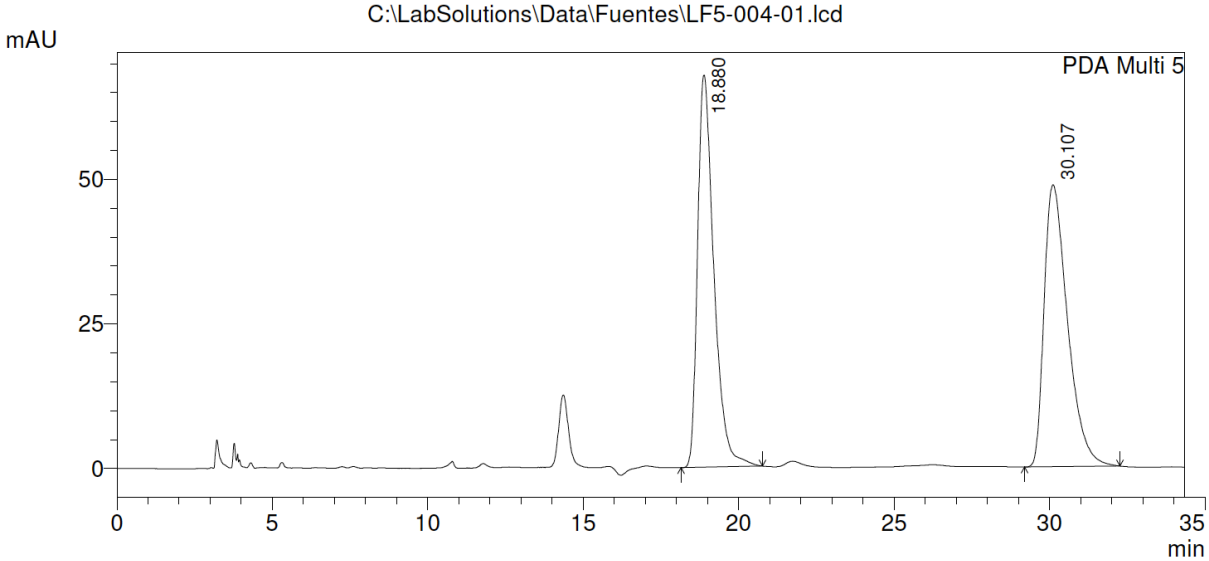
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.848	7743431	200541	50.509	59.646
2	29.963	7587340	135679	49.491	40.354
Total		15330771	336220	100.000	100.000

Enantioenriched ***Exo*-30** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



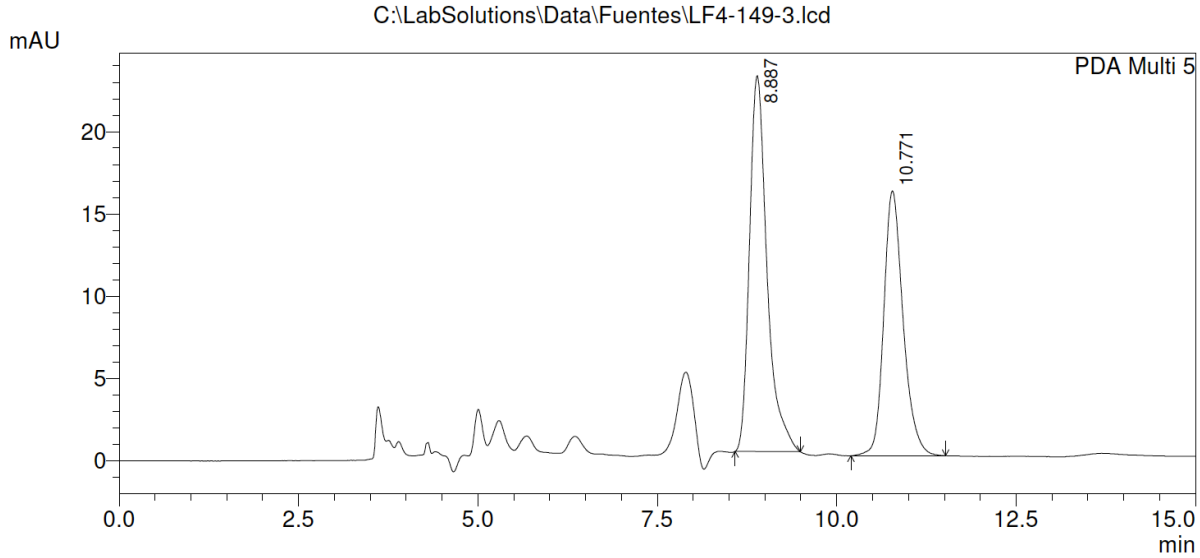
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.880	2465971	67753	49.089	58.148
2	30.107	2557515	48765	50.911	41.852
Total		5023486	116518	100.000	100.000

Racemic ***Endo*-31** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)



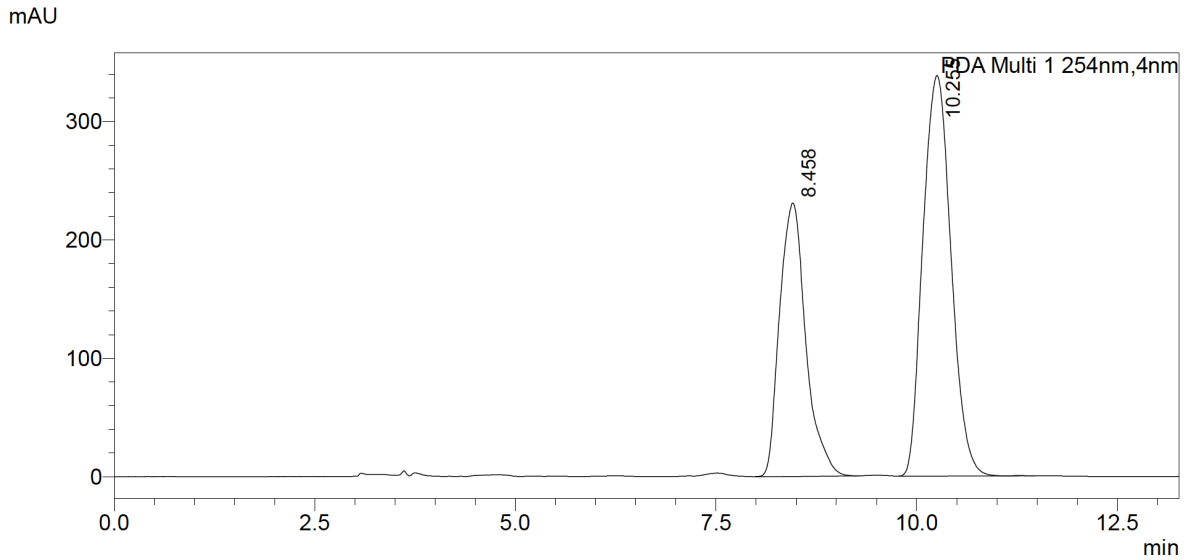
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.887	387775	22837	56.163	58.638
2	10.771	302676	16109	43.837	41.362
Total		690451	38946	100.000	100.000

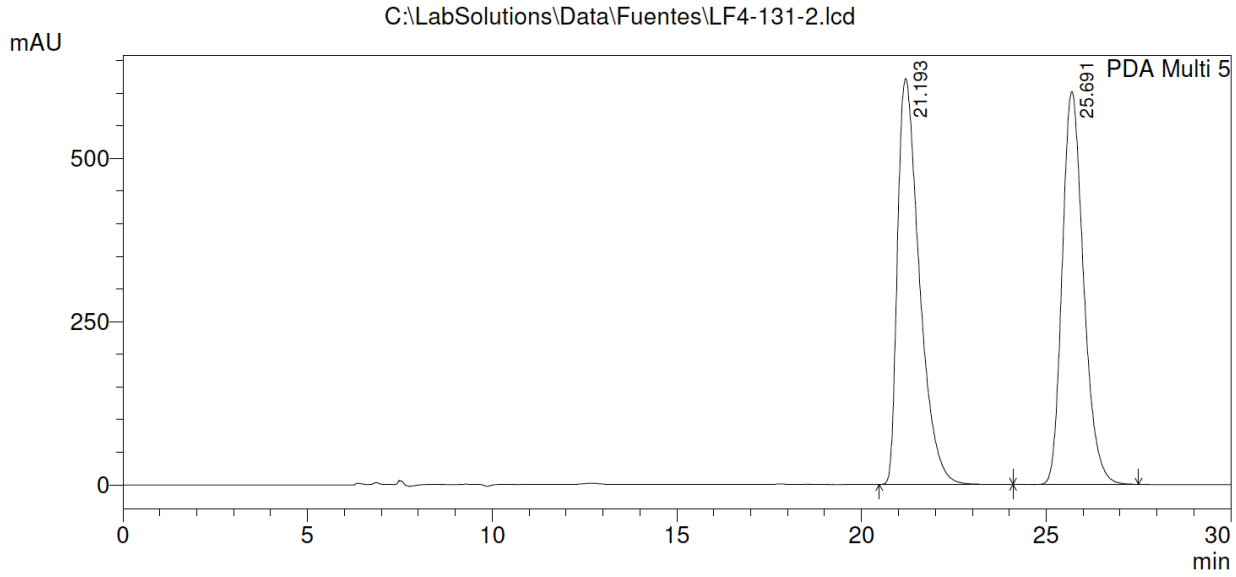
Enantioenriched ***Endo*-31** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.458	5238594	231106	38.798	40.570
2	10.255	8263782	338547	61.202	59.430
Total		13502376	569653	100.000	100.000

Racemic ***Endo*-32** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)



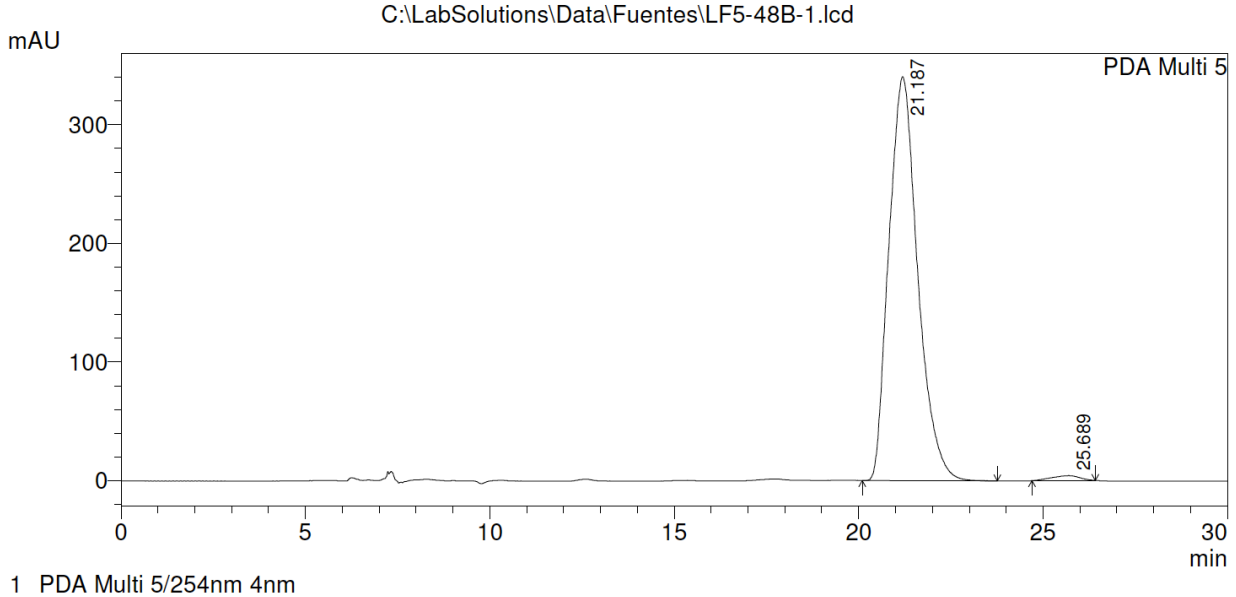
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.193	25489356	621522	51.261	50.816
2	25.691	24235125	601561	48.739	49.184
Total		49724481	1223083	100.000	100.000

Enantioenriched ***Endo*-32** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)



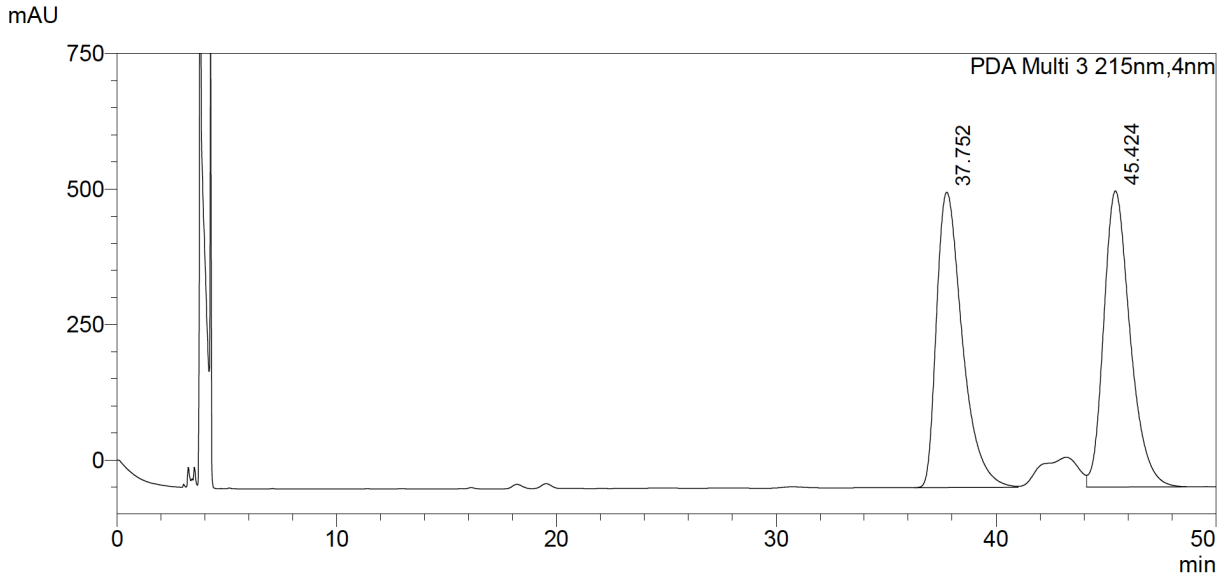
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.187	18521991	340585	98.839	98.802
2	25.689	217473	4130	1.161	1.198
Total		18739464	344715	100.000	100.000

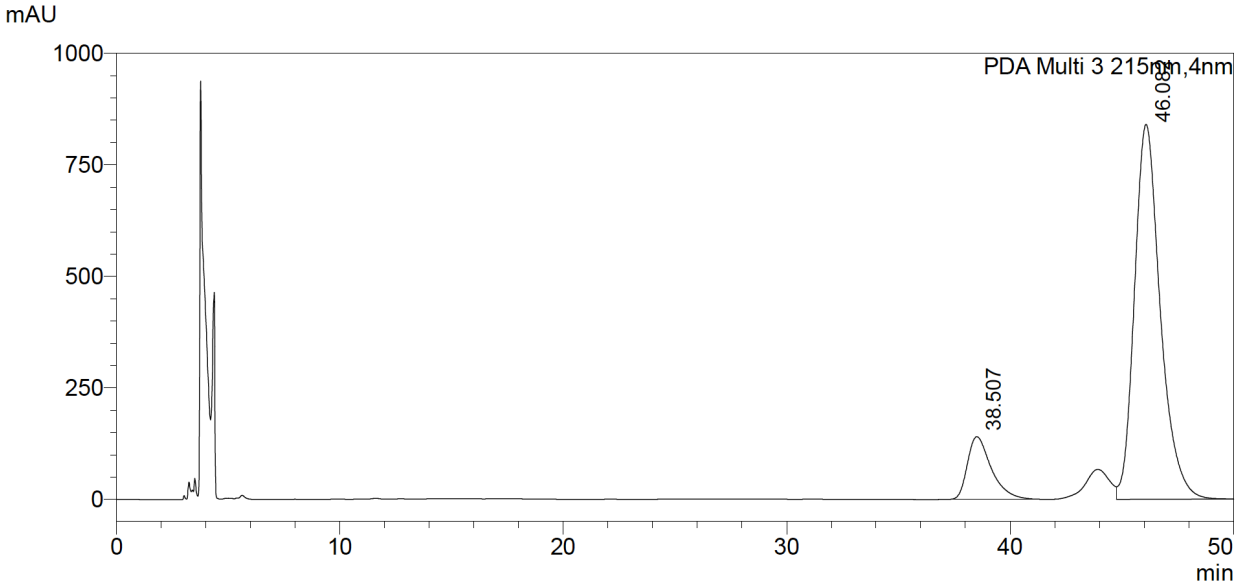
Racemic ***Exo*-32** (Chiralpak AD-H, Hexanes/*i*PrOH 97:3, 215 nm)



PDA Ch3 215nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	37.752	44454281	545091	49.361	49.950
2	45.424	45605683	546184	50.639	50.050
Total		90059965	1091274	100.000	100.000

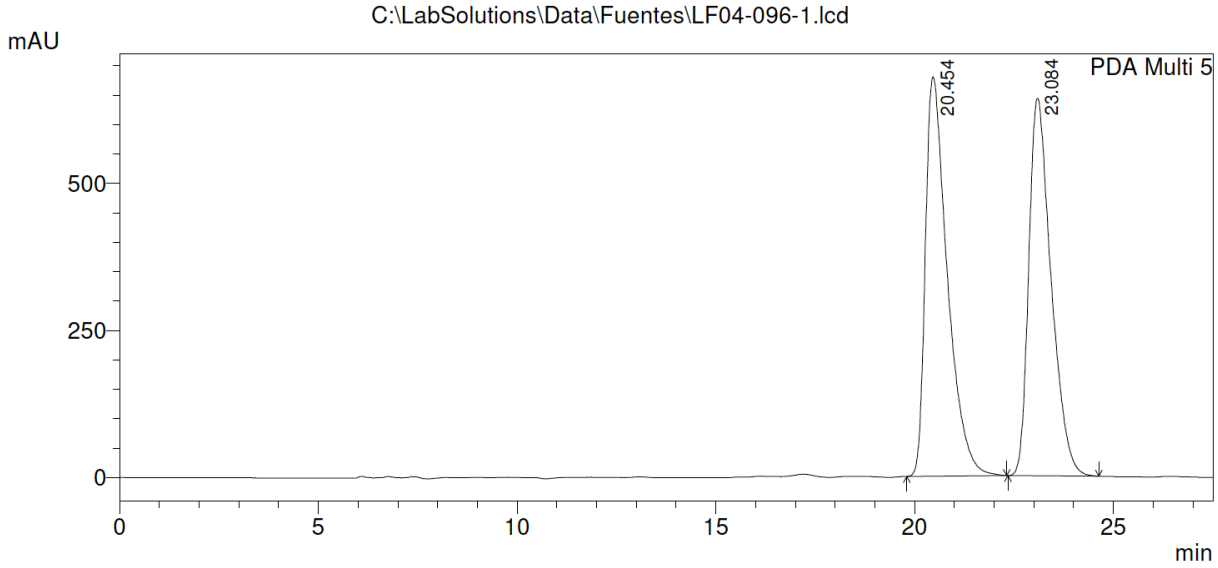
Enantioenriched ***Exo*-32** (Chiralpak AD-H, Hexanes/*i*PrOH 97:3, 215 nm)



PDA Ch3 215nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	38.507	10474740	140664	13.415	14.337
2	46.082	67608682	840491	86.585	85.663
Total		78083422	981155	100.000	100.000

Racemic ***Endo*-33** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



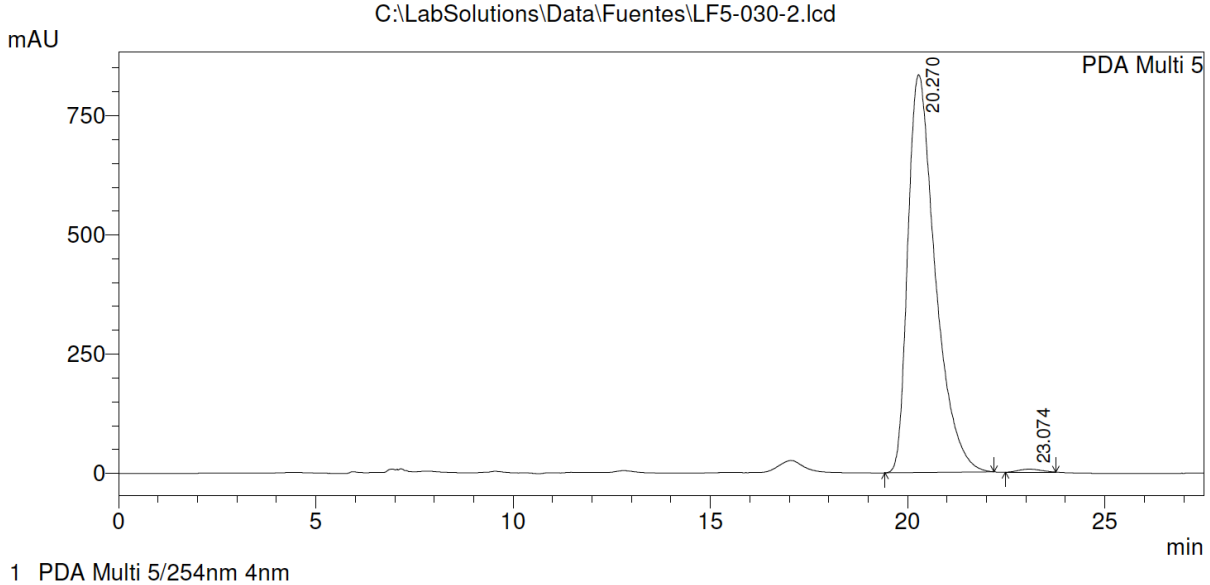
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.454	26084674	679301	51.002	51.416
2	23.084	25059770	641879	48.998	48.584
Total		51144444	1321180	100.000	100.000

Enantioenriched ***Endo*-33** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



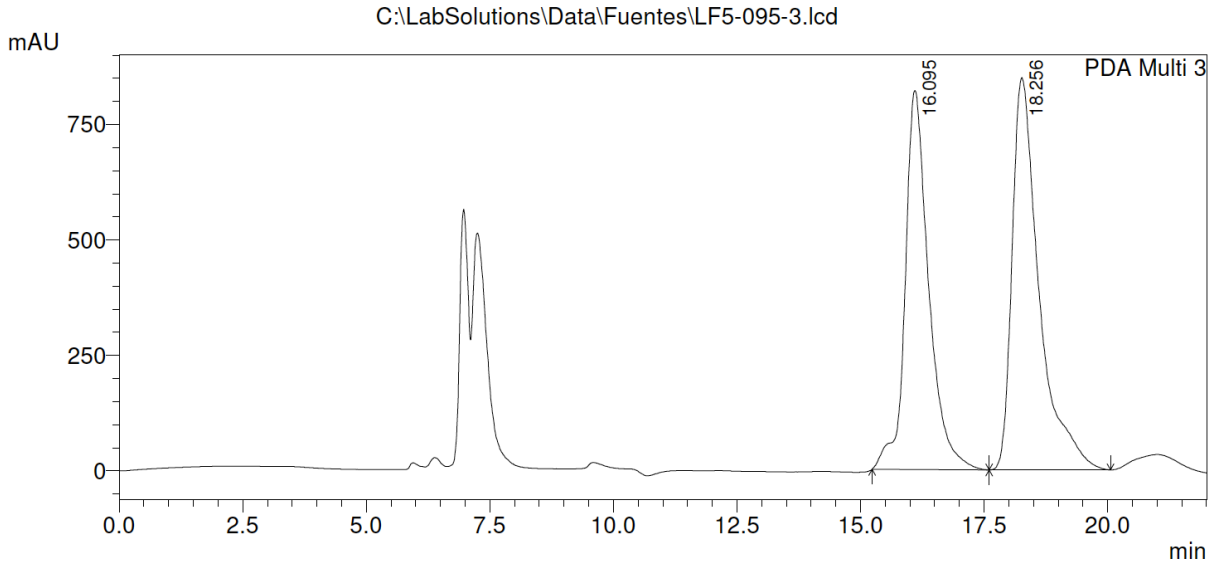
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.270	40317539	834739	99.388	99.252
2	23.074	248399	6291	0.612	0.748
Total		40565938	841030	100.000	100.000

Racemic ***Exo*-33** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 215 nm)



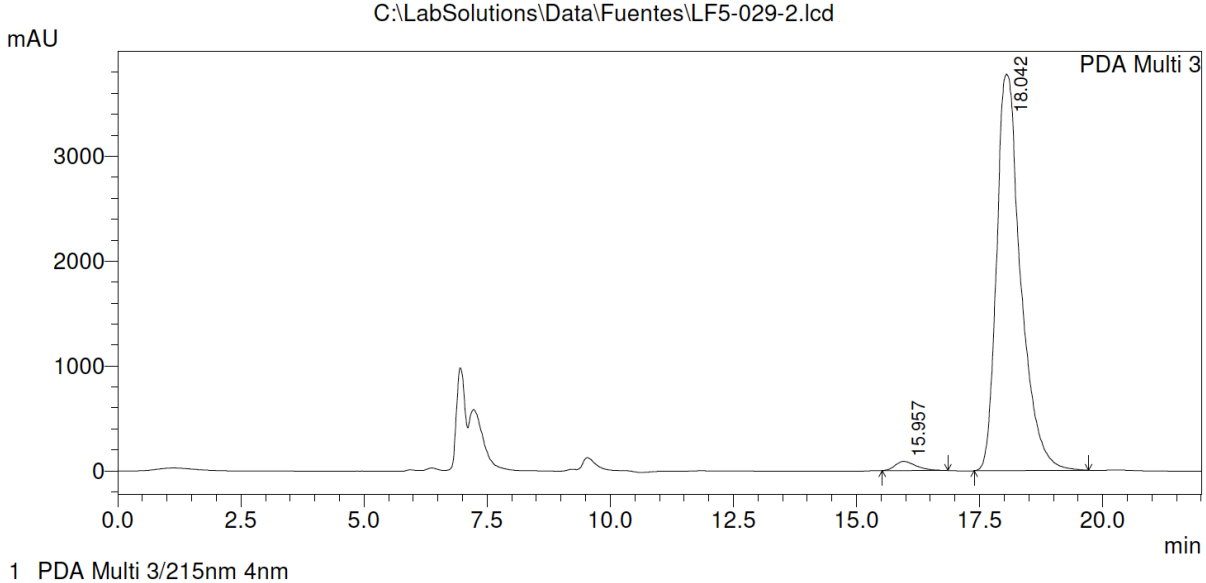
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.095	27295212	820986	45.869	49.129
2	18.256	32211134	850099	54.131	50.871
Total		59506347	1671085	100.000	100.000

Enantioenriched ***Exo*-33** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 215 nm)



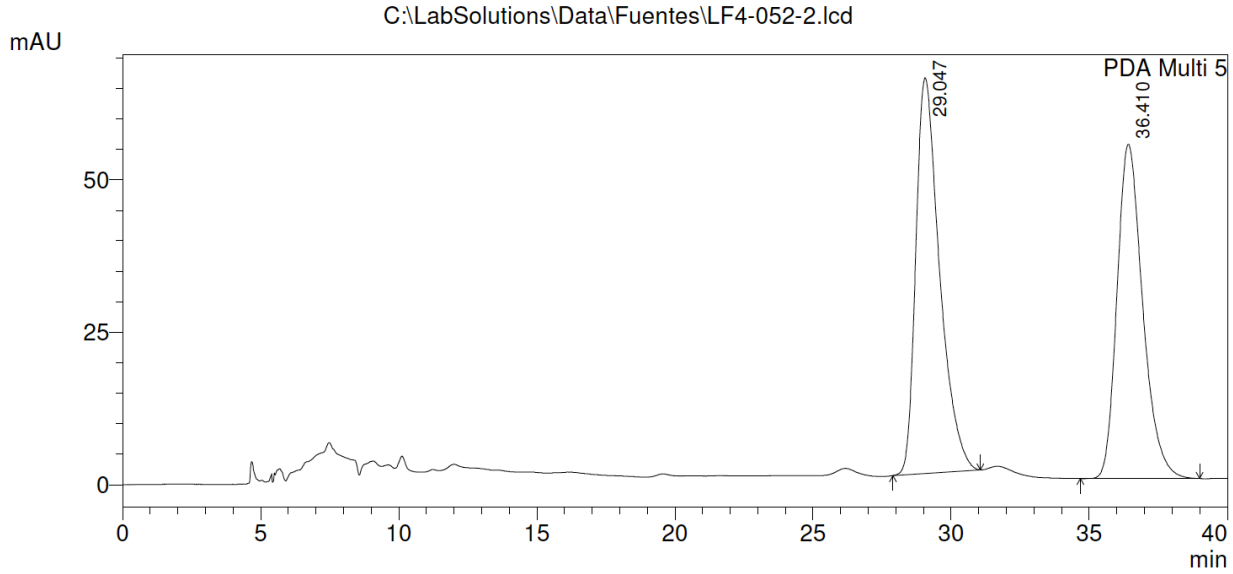
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.957	2555408	86561	1.949	2.238
2	18.042	128525507	3782020	98.051	97.762
Total		131080915	3868581	100.000	100.000

Racemic ***Endo*-34** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)

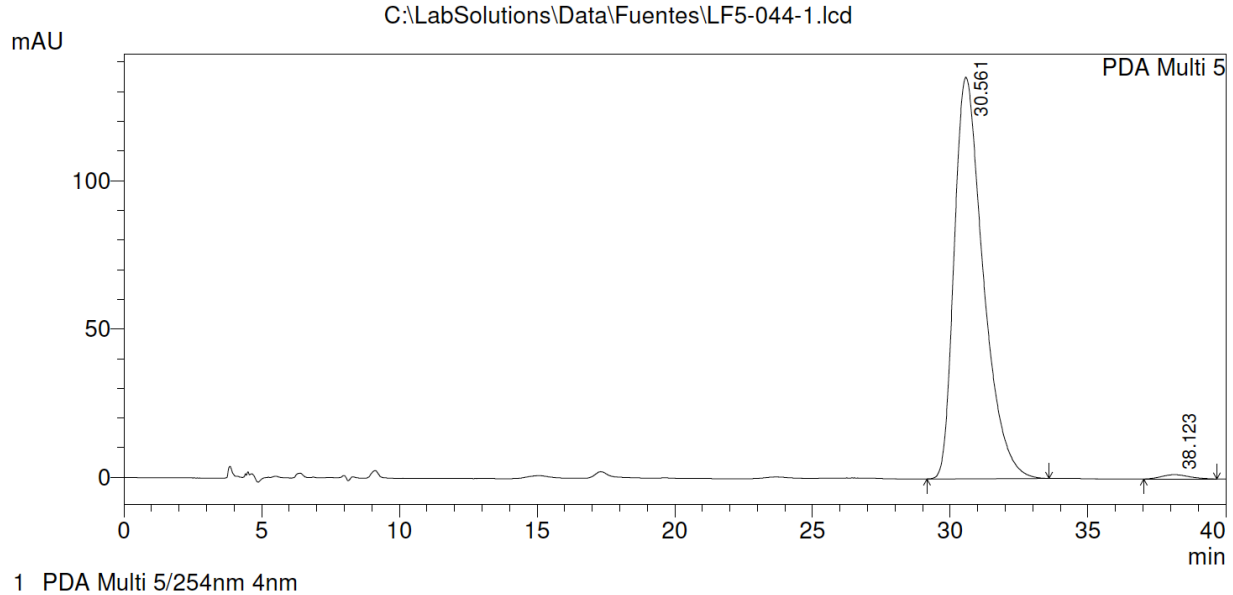


PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.047	3887734	64921	52.266	54.197
2	36.410	3550634	54866	47.734	45.803
Total		7438367	119787	100.000	100.000

Enantioenriched ***Endo*-34** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)

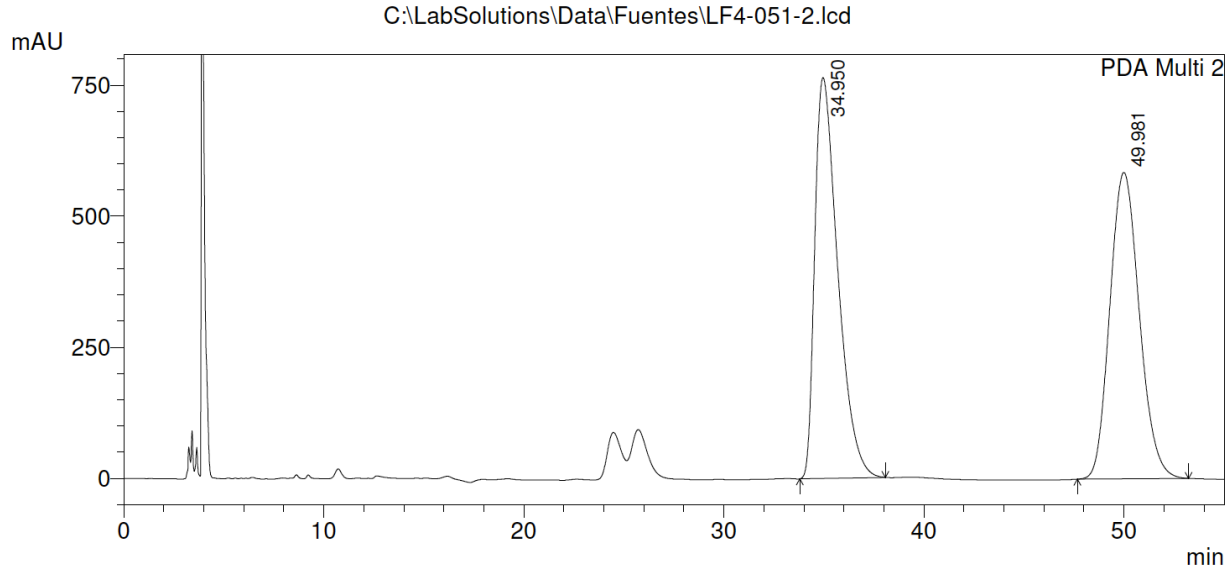


PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.561	9891240	135294	98.992	98.940
2	38.123	100731	1450	1.008	1.060
Total		9991972	136744	100.000	100.000

Racemic ***Exo*-34** (Chiralcel OD-H, Hexanes/*i*PrOH 90:10, 205 nm)

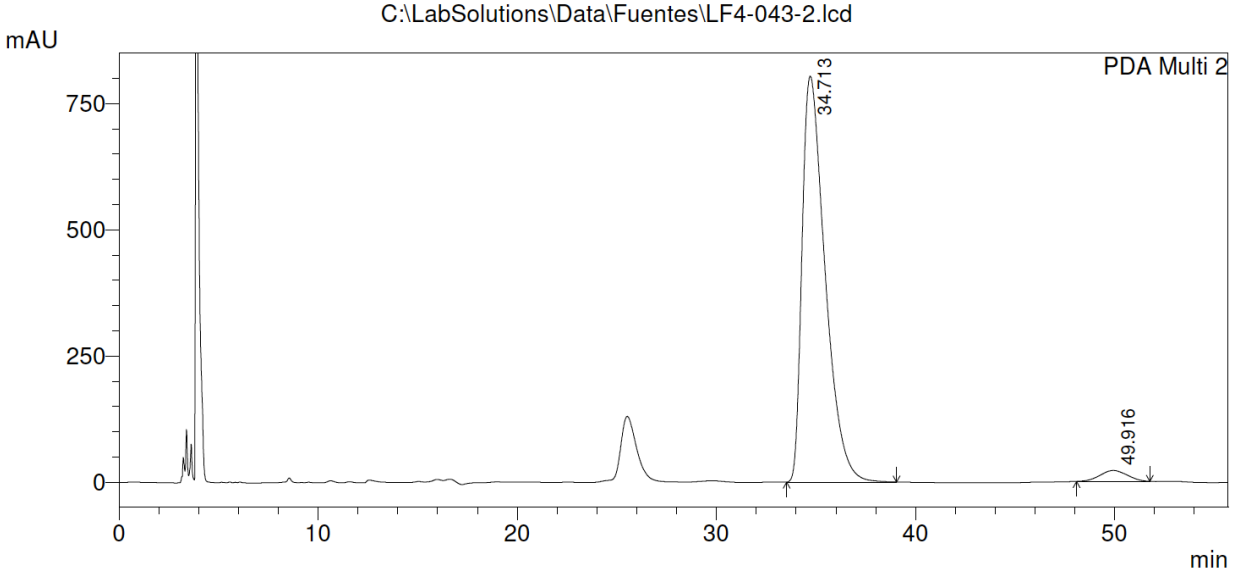


PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.950	61128309	764734	50.529	56.681
2	49.981	59848104	584447	49.471	43.319
Total		120976413	1349181	100.000	100.000

Enantioenriched ***Exo*-34** (Chiralcel OD-H, Hexanes/*i*PrOH 90:10, 205 nm)

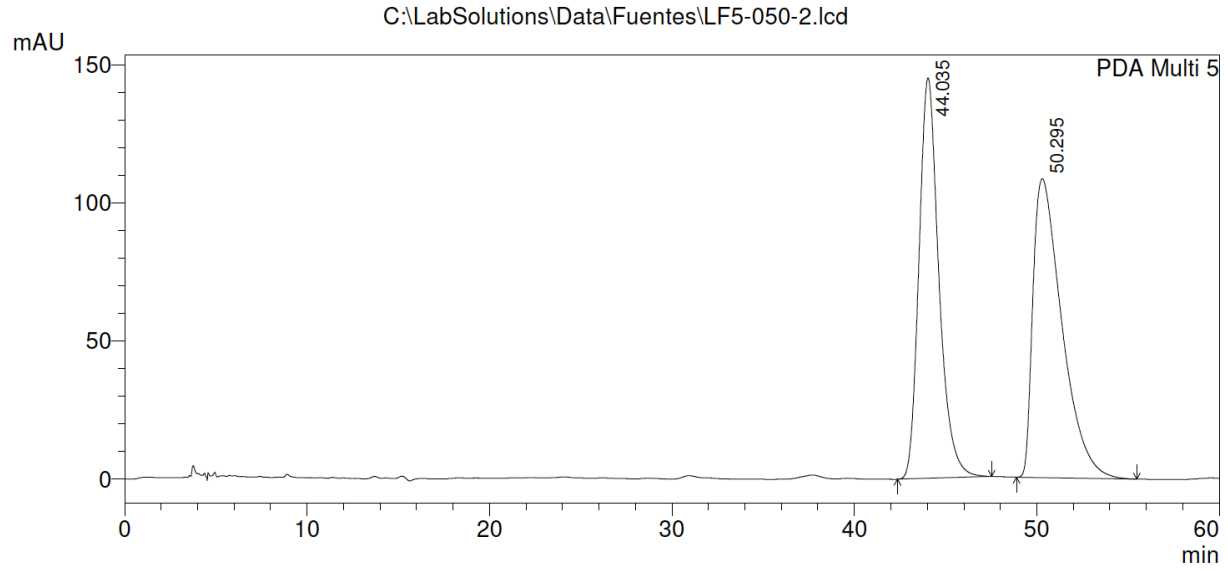


PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.713	64572698	803809	96.949	97.401
2	49.916	2032032	21451	3.051	2.599
Total		66604730	825260	100.000	100.000

Racemic ***Endo*-35** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



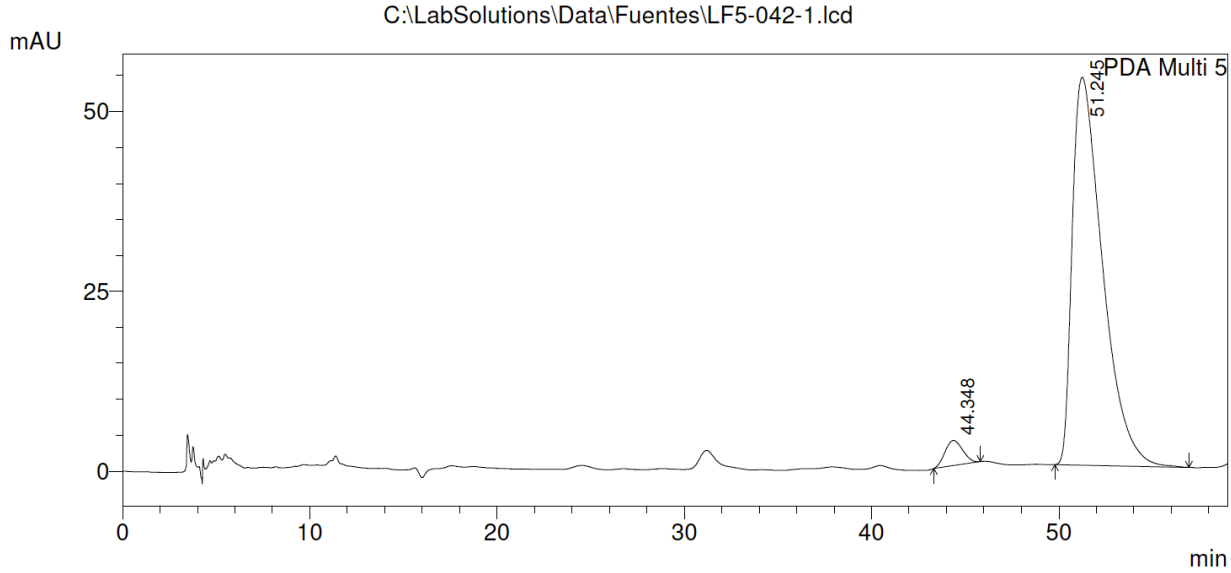
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.035	10971847	145002	47.880	57.259
2	50.295	11943420	108238	52.120	42.741
Total		22915267	253240	100.000	100.000

Enantioenriched ***Endo*-35** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



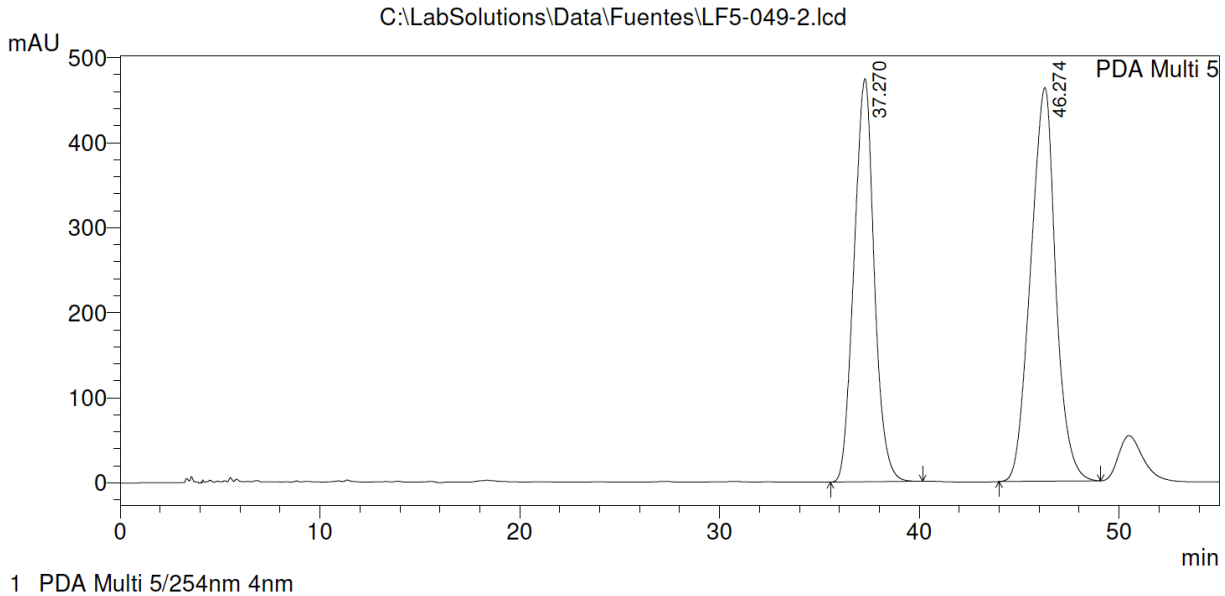
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.348	231004	3509	3.673	6.110
2	51.245	6059004	53931	96.327	93.890
Total		6290008	57440	100.000	100.000

Racemic ***Exo*-35** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



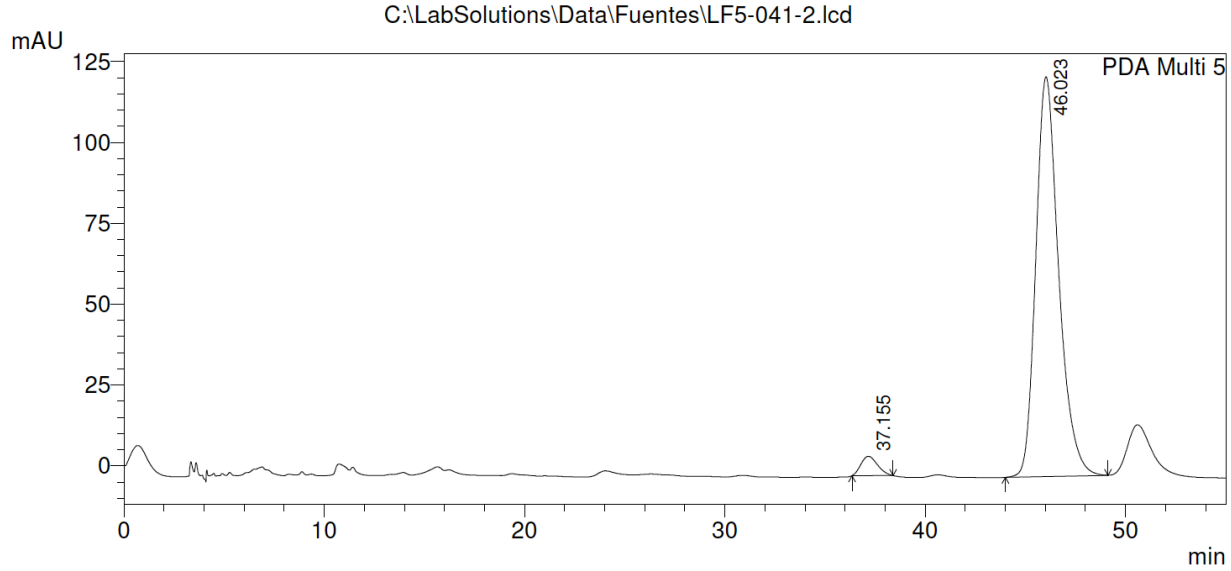
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.270	33293341	473780	45.246	50.583
2	46.274	40289897	462864	54.754	49.417
Total		73583238	936643	100.000	100.000

Enantioenriched ***Exo*-35** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



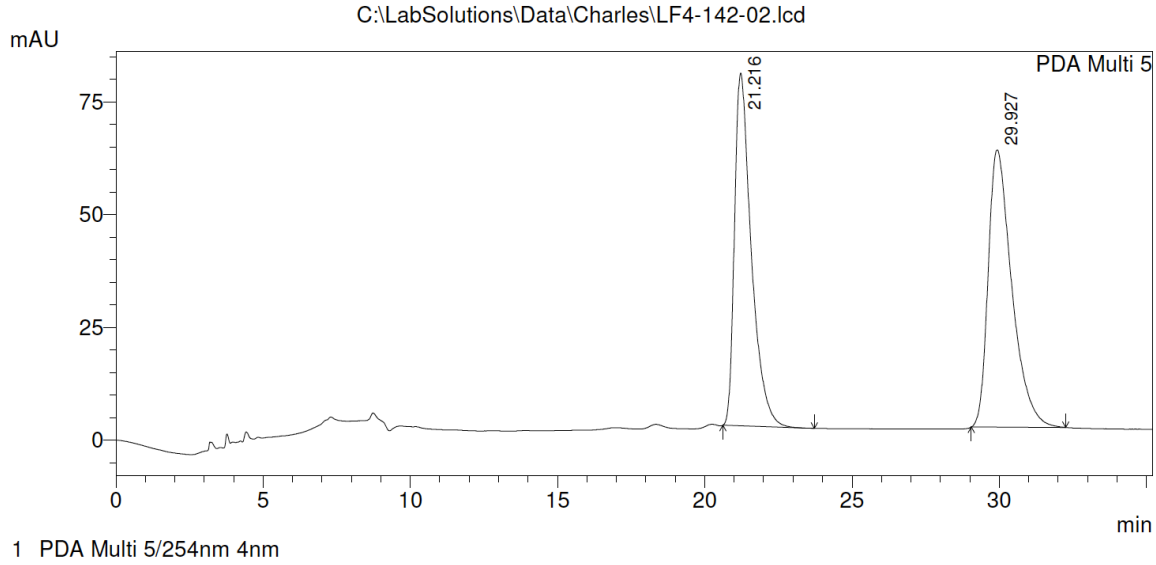
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.155	344839	6010	3.393	4.634
2	46.023	9819603	123672	96.607	95.366
Total		10164442	129681	100.000	100.000

Racemic ***Endo*-36** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



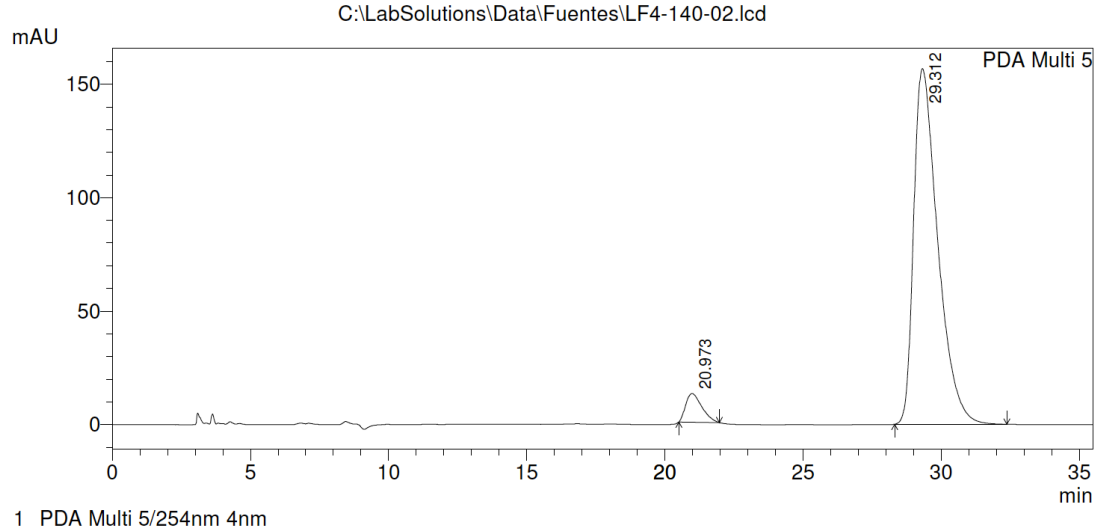
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.216	3096217	78135	47.456	55.983
2	29.927	3428145	61435	52.544	44.017
Total		6524362	139570	100.000	100.000

Enantioenriched ***Endo*-36** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



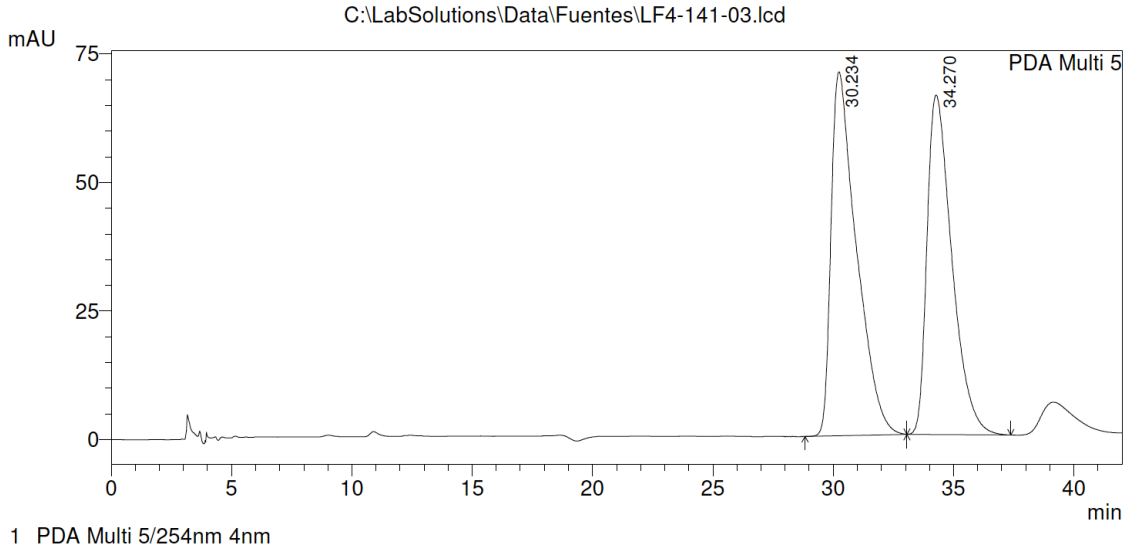
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.973	510519	12635	5.098	7.463
2	29.312	9503042	156653	94.902	92.537
Total		10013561	169288	100.000	100.000

Racemic ***Exo*-36** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)

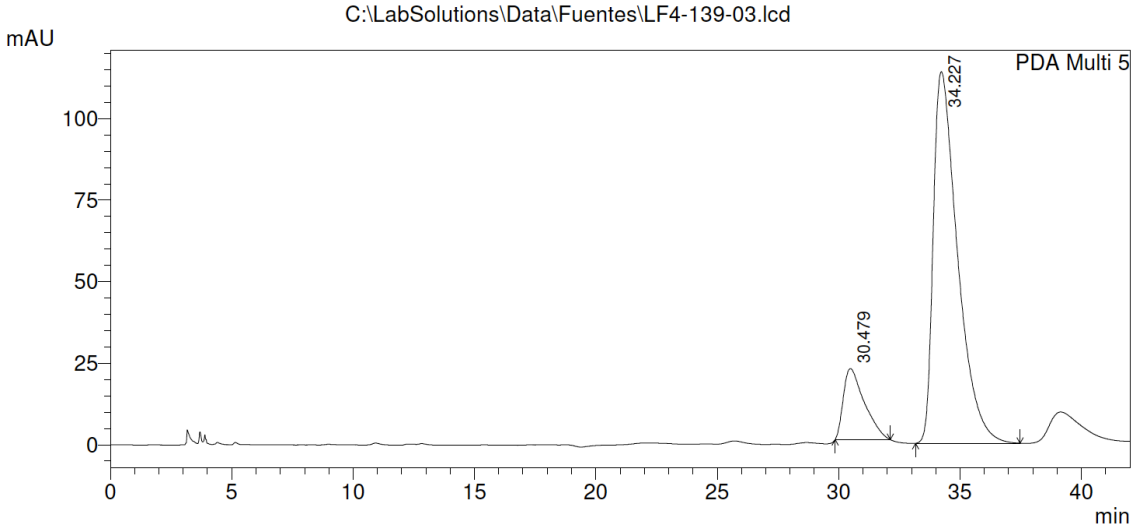


PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.234	5180178	70787	52.176	51.738
2	34.270	4748143	66033	47.824	48.262
Total		9928321	136820	100.000	100.000

Enantioenriched ***Exo*-36** (Chiralpak IA, Hexanes/*i*PrOH 95:5, 254 nm)

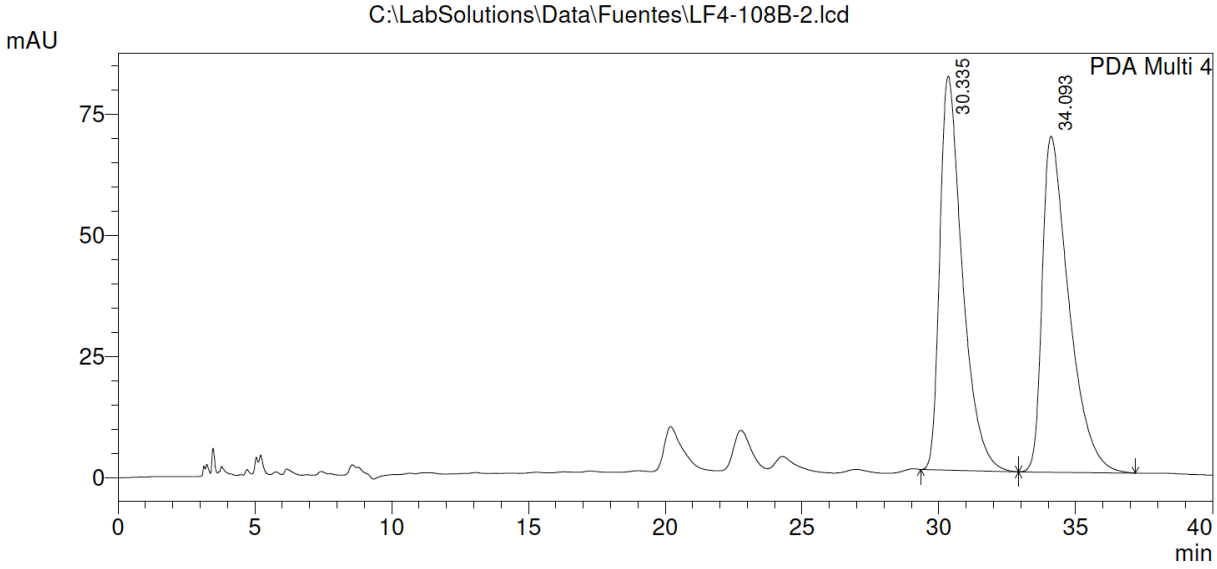


PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.479	1310605	21805	14.177	16.053
2	34.227	7933850	114024	85.823	83.947
Total		9244456	135829	100.000	100.000

Racemic ***Endo*-37** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 240 nm)



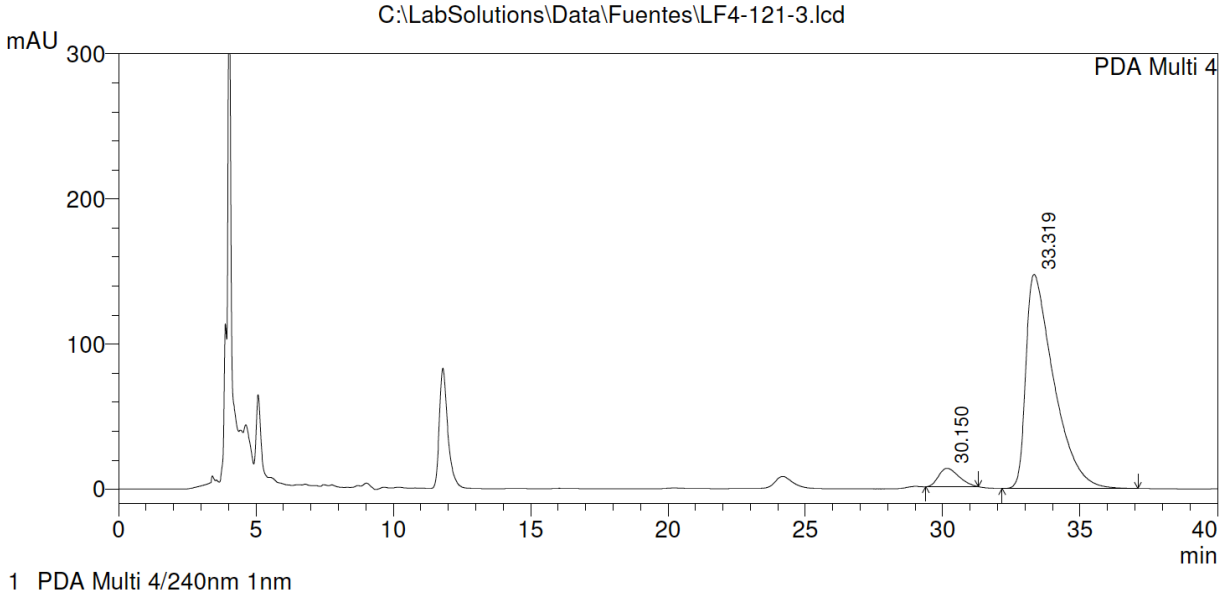
1 PDA Multi 4/240nm 1nm

PeakTable

PDA Ch4 240nm 1nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.335	4654265	81250	49.756	53.968
2	34.093	4699978	69301	50.244	46.032
Total		9354243	150552	100.000	100.000

Enantioenriched ***Endo*-37** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 240 nm)



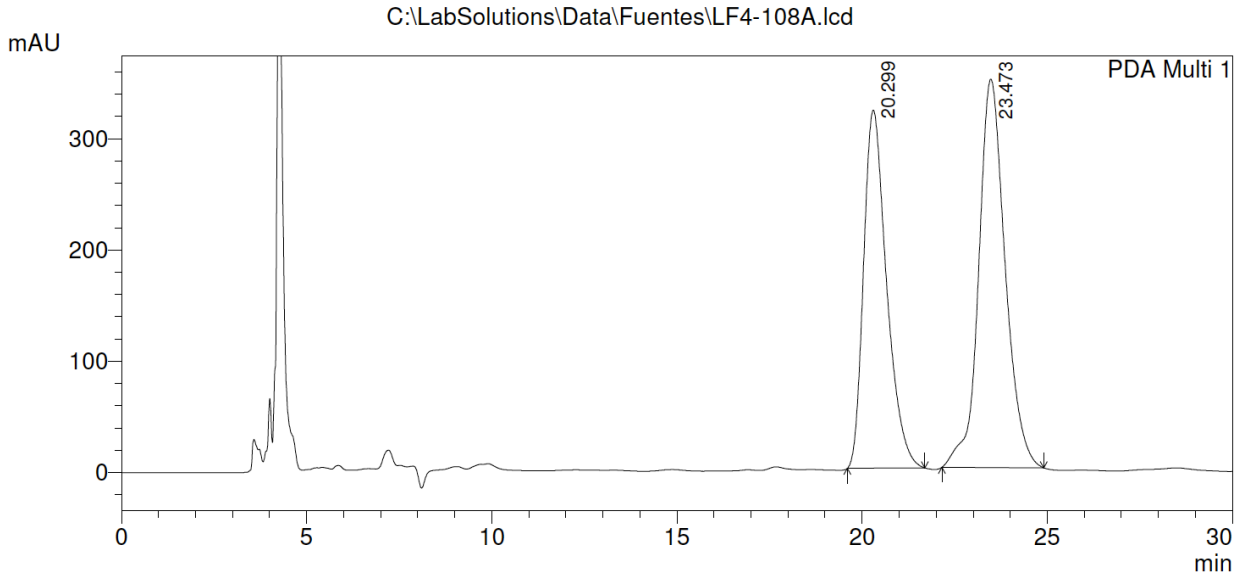
1 PDA Multi 4/240nm 1nm

PeakTable

PDA Ch4 240nm 1nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.150	653989	12711	5.908	7.926
2	33.319	10414971	147657	94.092	92.074
Total		11068960	160367	100.000	100.000

Racemic ***Exo*-37** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 215 nm)



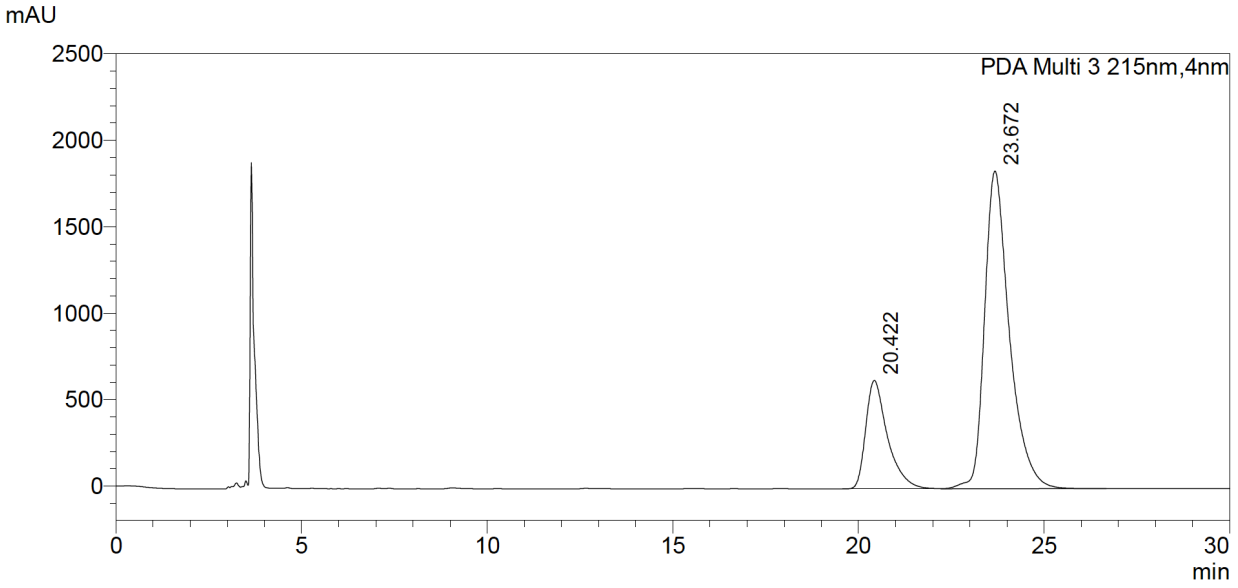
1 PDA Multi 1/215nm 4nm

PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.299	13919500	321665	44.449	47.966
2	23.473	17396187	348941	55.551	52.034
Total		31315688	670606	100.000	100.000

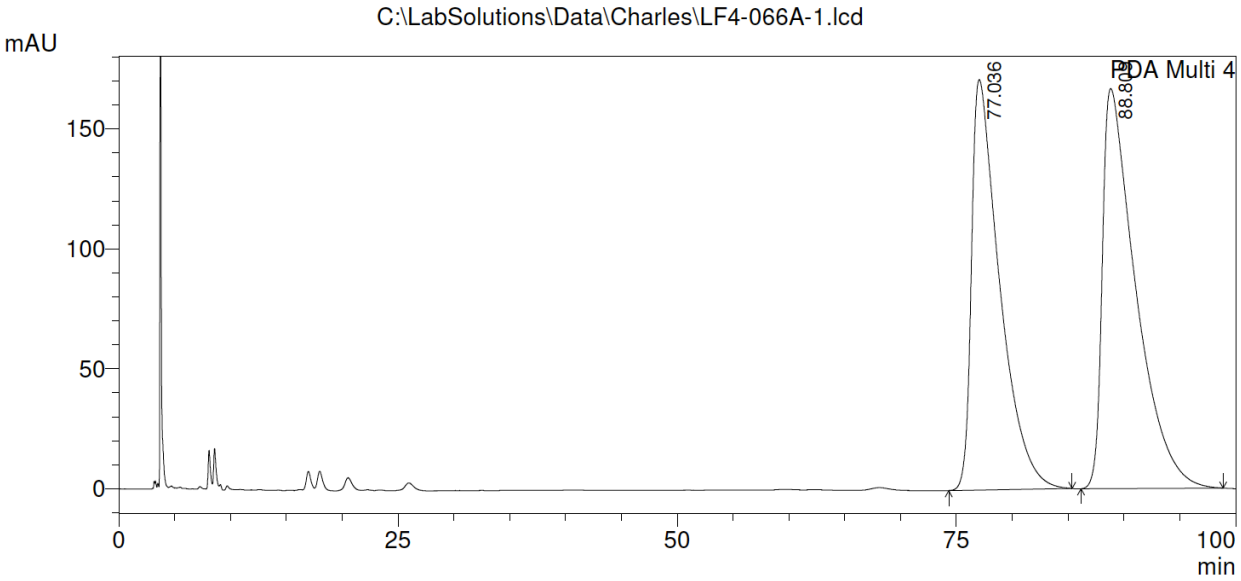
Enantioenriched ***Exo*-37** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 215 nm)



PDA Ch3 215nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.422	25581817	626685	23.046	25.439
2	23.672	85419367	1836778	76.954	74.561
Total		111001184	2463463	100.000	100.000

Racemic ***Endo*-38** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 240 nm)



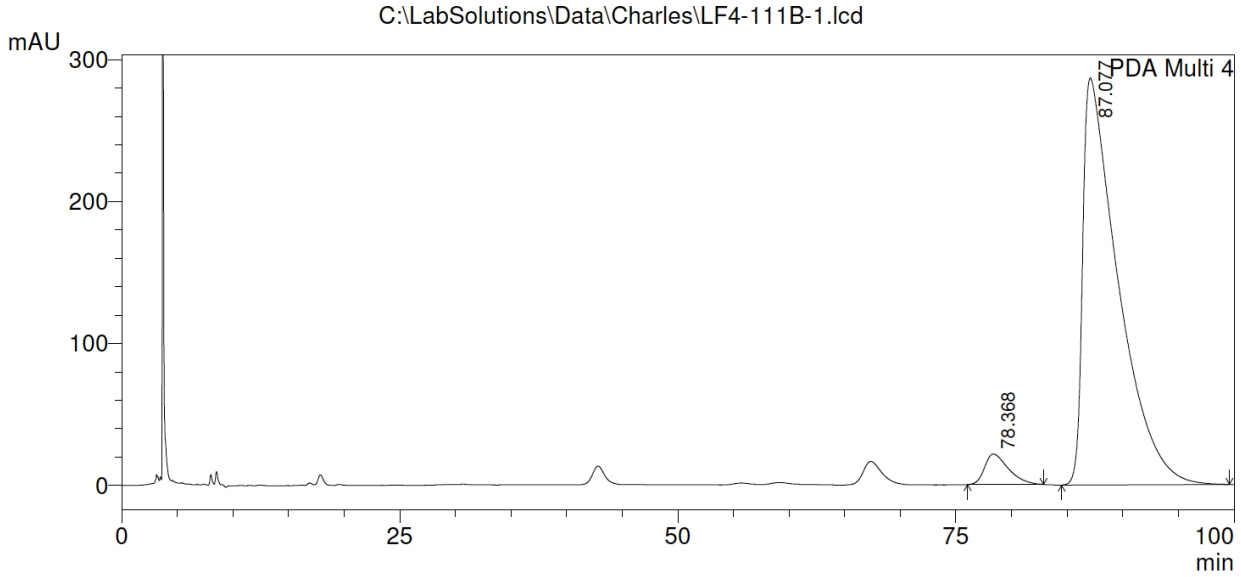
1 PDA Multi 4/240nm 1nm

PeakTable

PDA Ch4 240nm 1nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	77.036	30026202	170982	46.449	50.642
2	88.809	34616570	166649	53.551	49.358
Total		64642771	337630	100.000	100.000

Enantioenriched ***Endo*-38** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 240 nm)



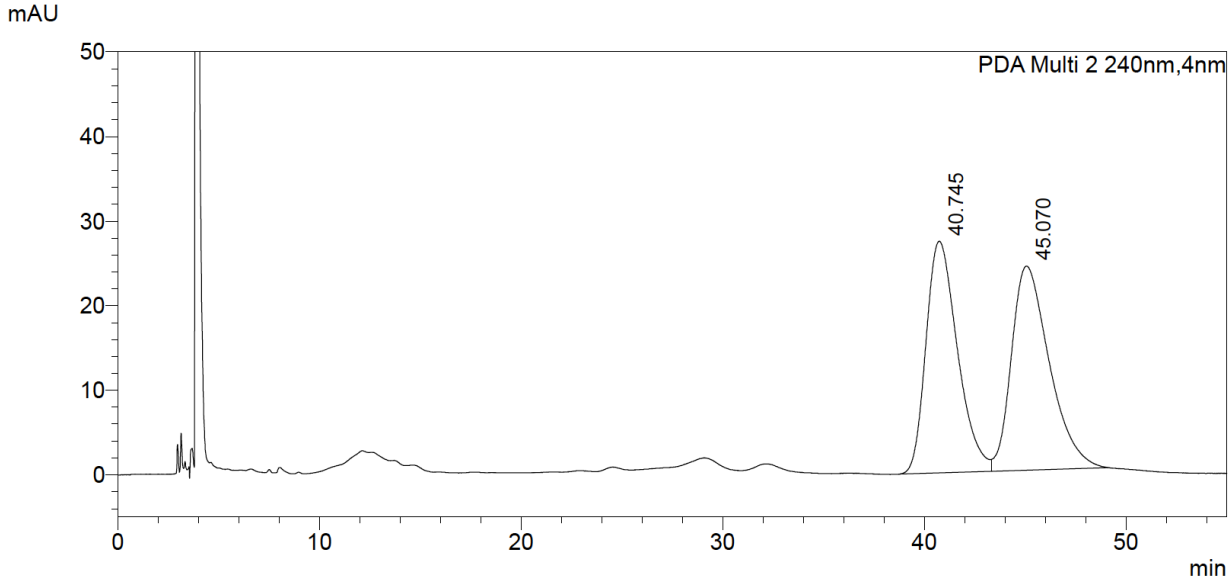
1 PDA Multi 4/240nm 1nm

PeakTable

PDA Ch4 240nm 1nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	78.368	3210085	21464	4.817	6.970
2	87.077	63425016	286499	95.183	93.030
Total		66635101	307964	100.000	100.000

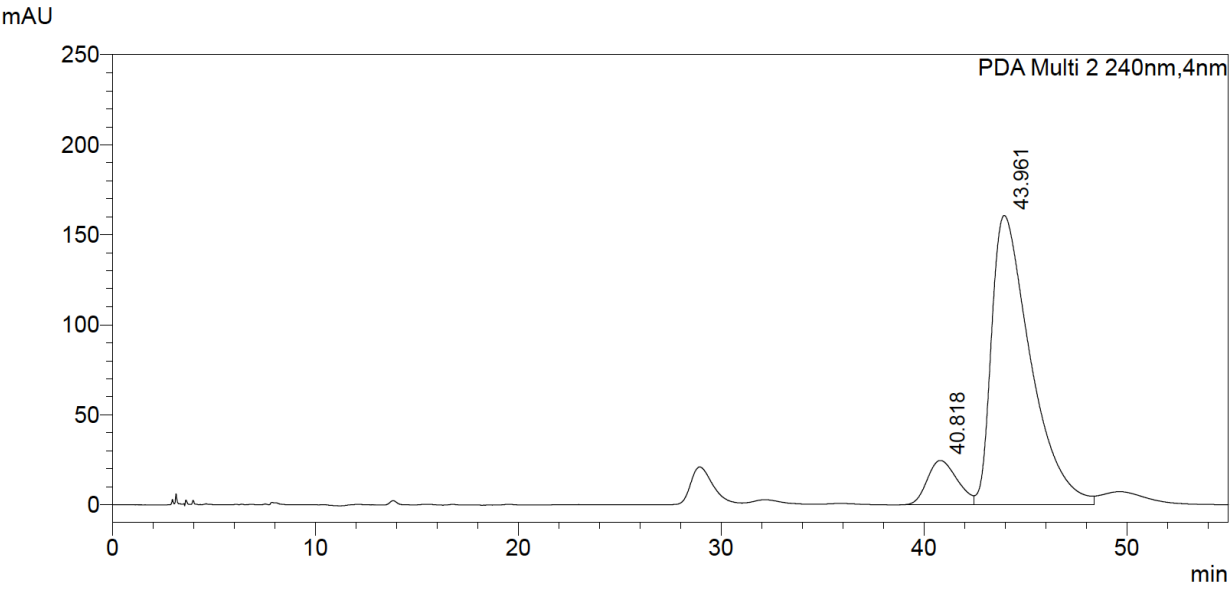
Racemic ***Exo*-38** (Chiralpak OD-H, Hexanes/*i*PrOH 85:15, 240 nm)



PDA Ch2 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	40.745	2976772	27405	48.484	53.172
2	45.070	3162891	24135	51.516	46.828
Total		6139663	51541	100.000	100.000

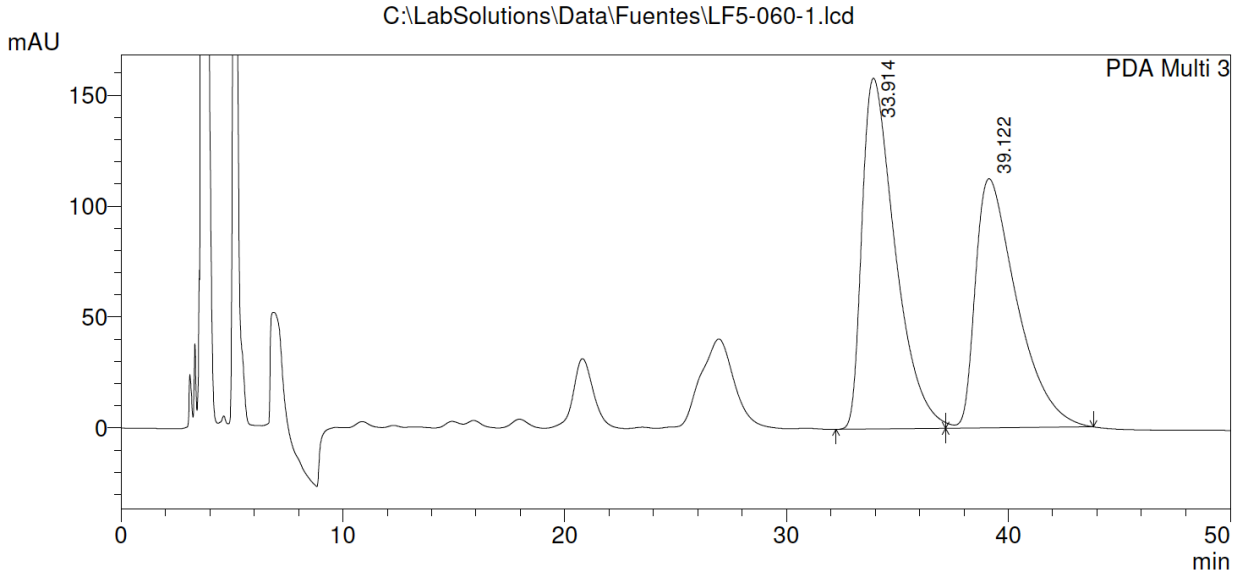
Enantioenriched ***Exo*-38** (Chiralpak OD-H, Hexanes/*i*PrOH 85:15, 240 nm)



PDA Ch2 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	40.818	2520500	24623	10.486	13.283
2	43.961	21515862	160754	89.514	86.717
Total		24036362	185378	100.000	100.000

Racemic ***Endo*-39** (Chiralpak OD-H, Hexanes/*i*PrOH 80:20, 215 nm)



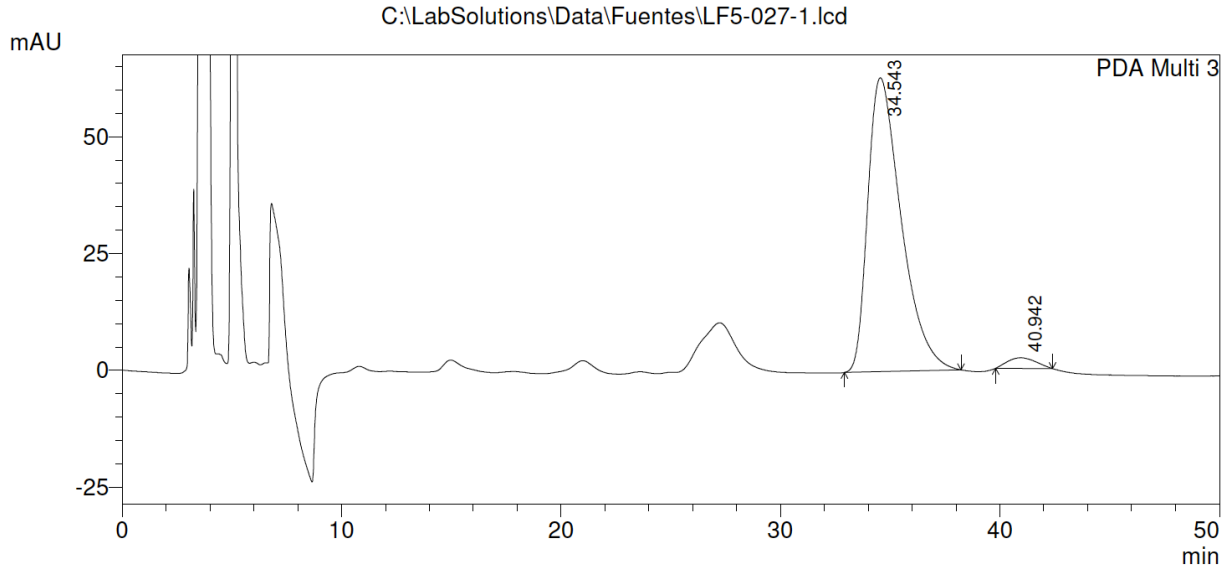
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.914	16449145	158000	53.000	58.471
2	39.122	14587018	112221	47.000	41.529
Total		31036162	270220	100.000	100.000

Enantioenriched ***Endo*-39** (Chiralpak OD-H, Hexanes/*i*PrOH 80:20, 215 nm)



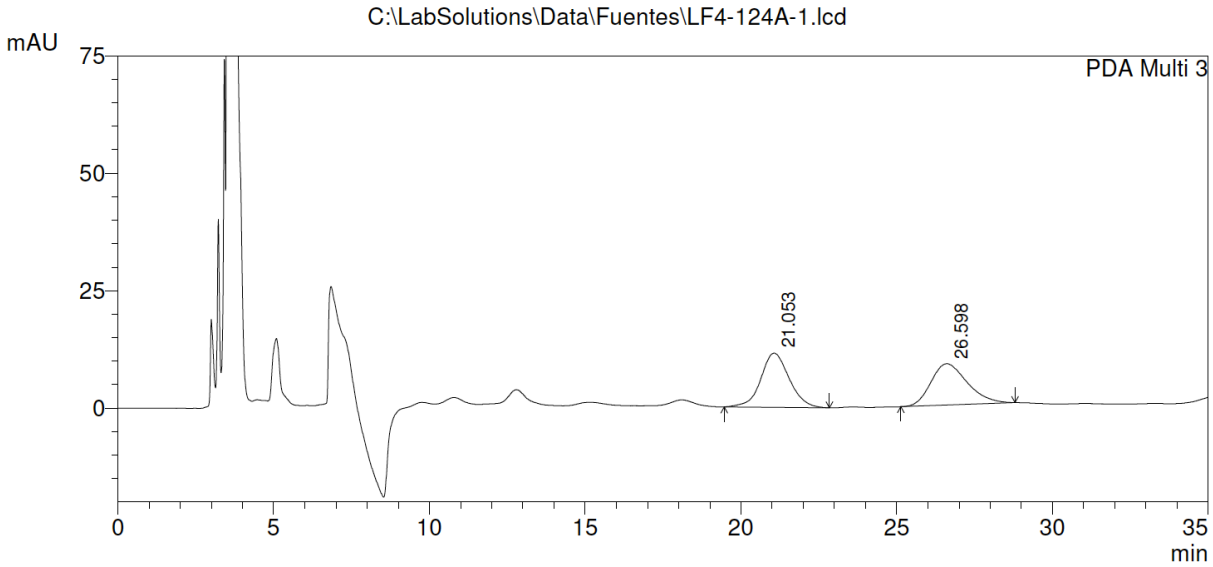
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.543	6656396	62889	97.033	96.536
2	40.942	203531	2257	2.967	3.464
Total		6859927	65146	100.000	100.000

Racemic ***Exo*-39** (Chiralpak OD-H, Hexanes/*i*PrOH 80:20, 215 nm)

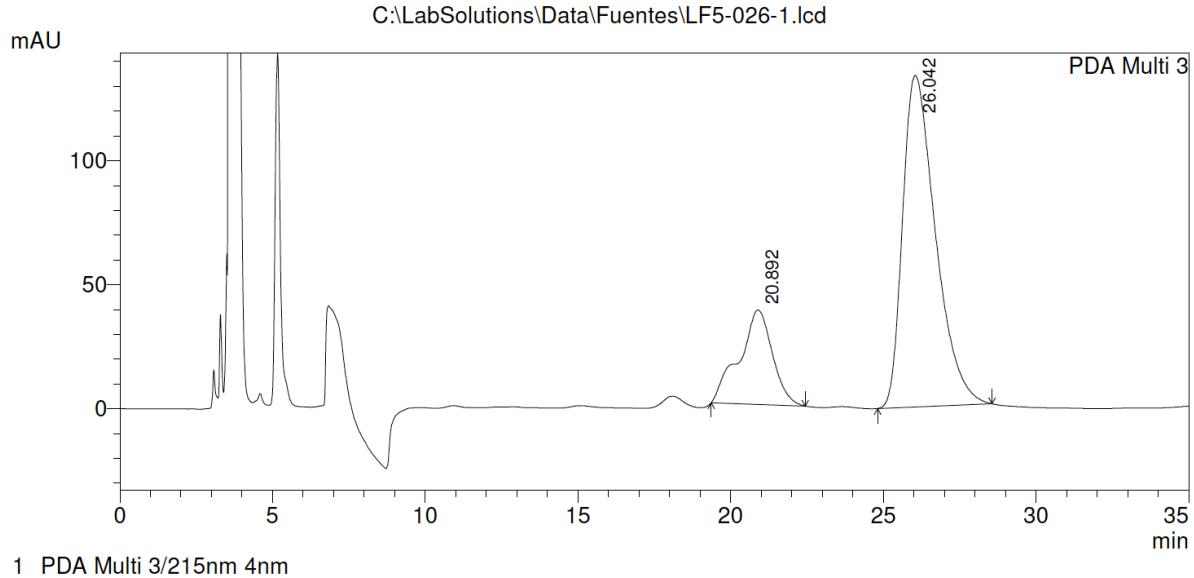


PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.053	733664	11538	50.642	56.712
2	26.598	715065	8807	49.358	43.288
Total		1448729	20345	100.000	100.000

Enantioenriched ***Exo*-39** (Chiralpak OD-H, Hexanes/*i*PrOH 80:20, 215 nm)

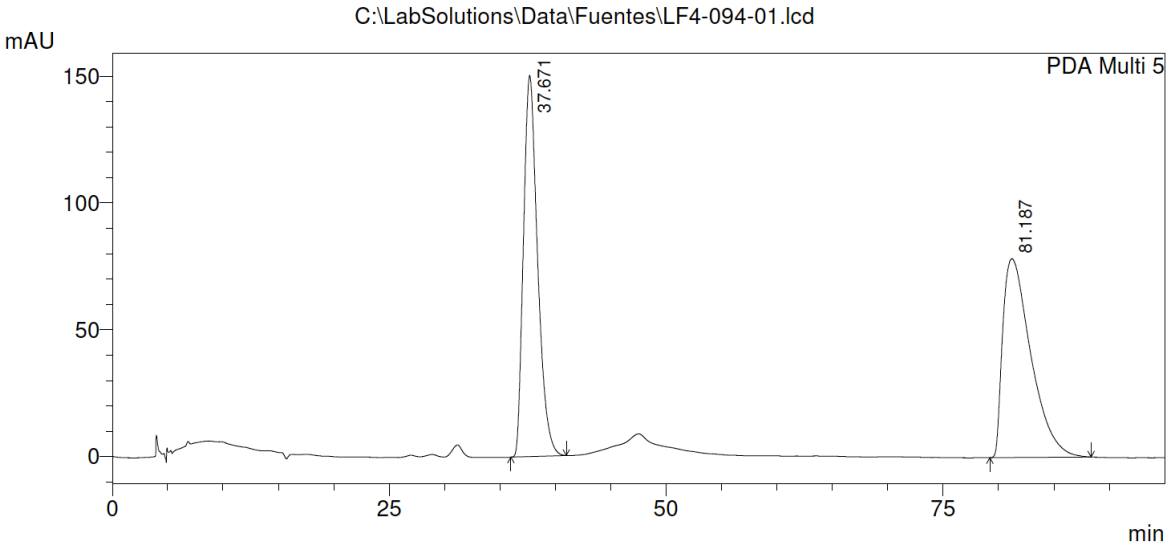


PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.892	2883062	38093	22.362	22.181
2	26.042	10009498	133647	77.638	77.819
Total		12892560	171740	100.000	100.000

Racemic ***Endo*-40** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)



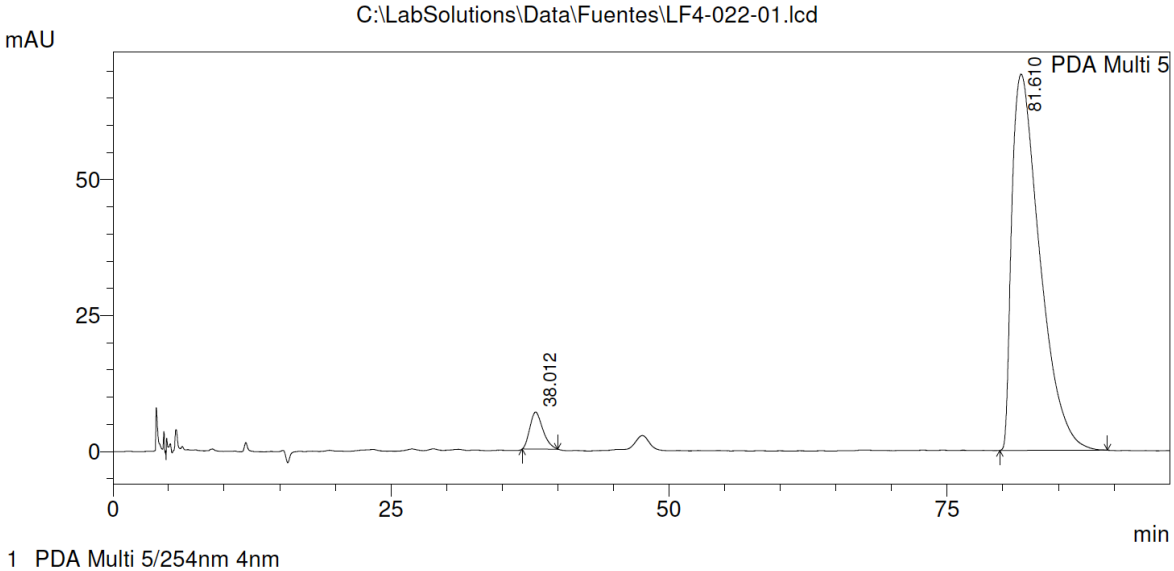
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.671	13340007	150462	49.033	65.717
2	81.187	13866256	78493	50.967	34.283
Total		27206263	228955	100.000	100.000

Enantioenriched ***Endo*-40** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 254 nm)



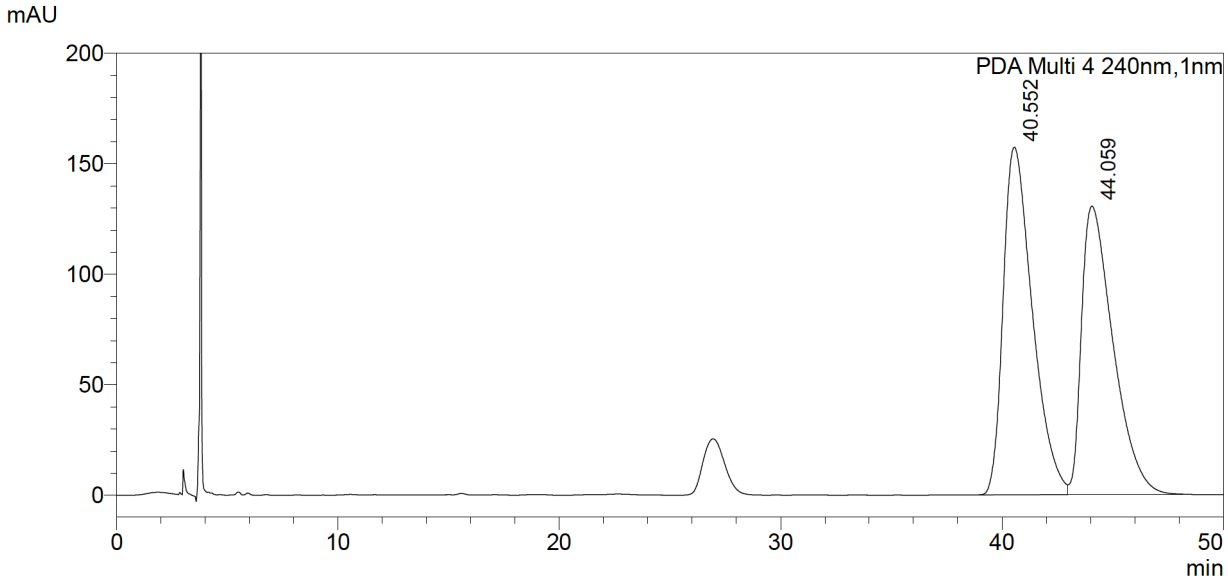
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.012	552493	6806	4.367	8.955
2	81.610	12100390	69191	95.633	91.045
Total		12652883	75996	100.000	100.000

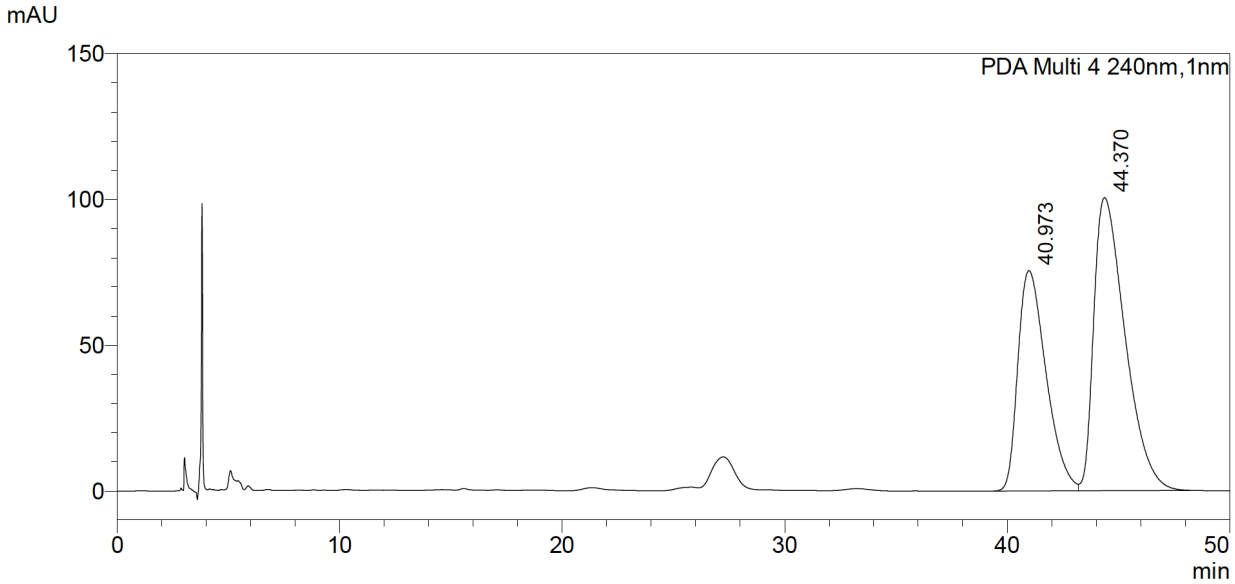
Racemic ***Exo*-40** (Chiralpak OD-H, Hexanes/*i*PrOH 95:5, 240 nm)



PDA Ch4 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	40.552	14459671	157318	52.698	54.644
2	44.059	12979190	130579	47.302	45.356
Total		27438861	287897	100.000	100.000

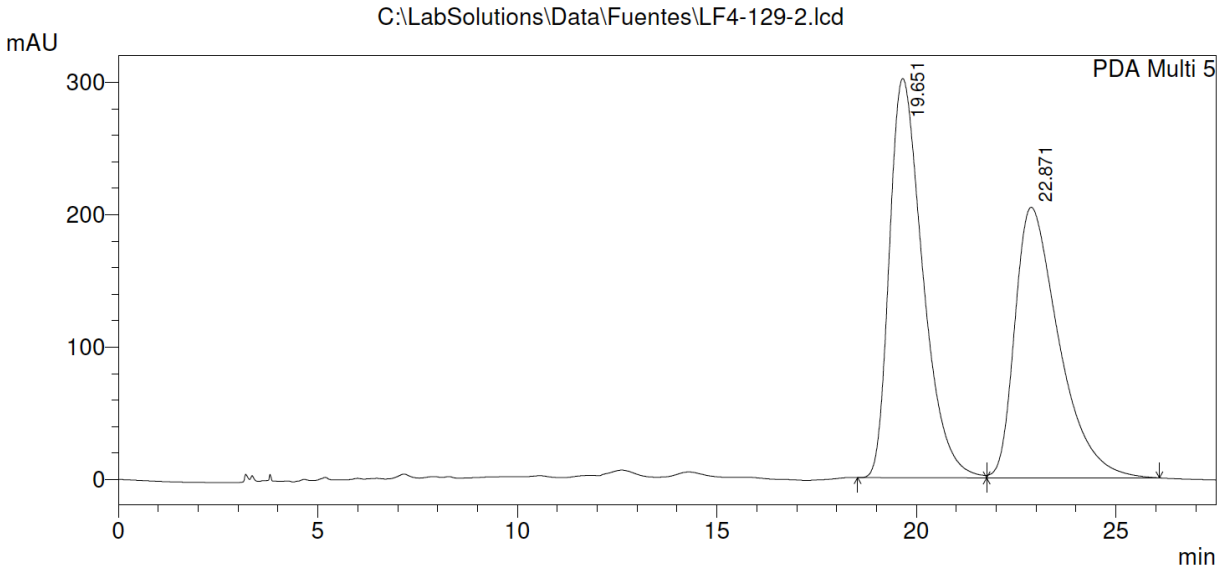
Enantioenriched ***Exo*-40** (Chiralpak OD-H, Hexanes/*i*PrOH 95:5, 240 nm)



PDA Ch4 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	40.973	6654577	75560	40.351	42.914
2	44.370	9837007	100512	59.649	57.086
Total		16491584	176072	100.000	100.000

Racemic ***Endo*-41** (Chiralpak OD-H, Hexanes/*i*PrOH 90:10, 254 nm)



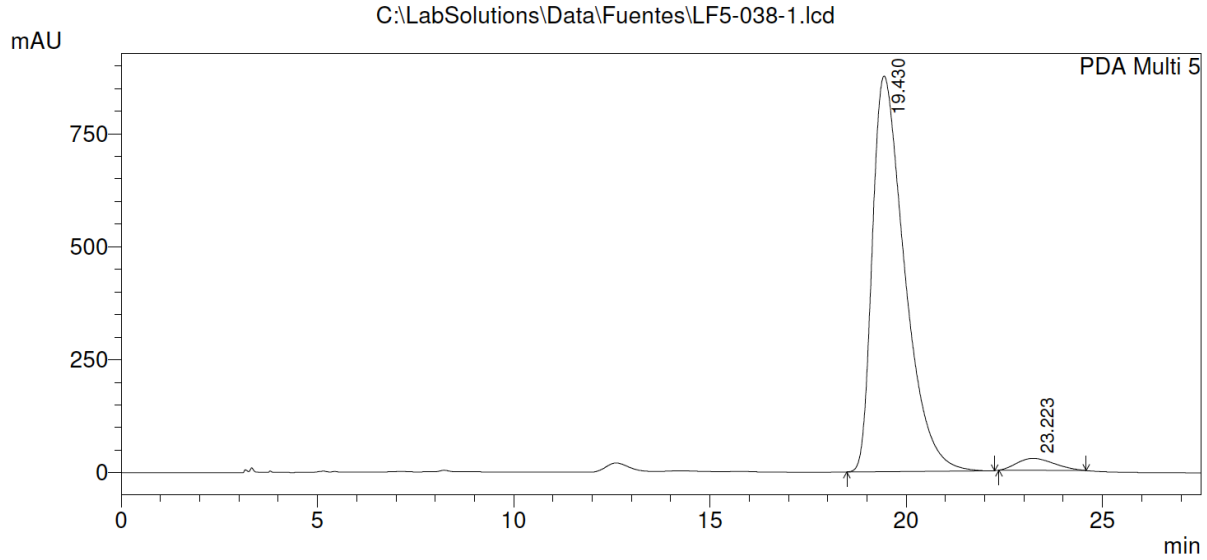
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.651	17529401	301587	52.754	59.603
2	22.871	15699446	204407	47.246	40.397
Total		33228846	505994	100.000	100.000

Enantioenriched ***Endo*-41** (Chiralpak OD-H, Hexanes/*i*PrOH 90:10, 254 nm)



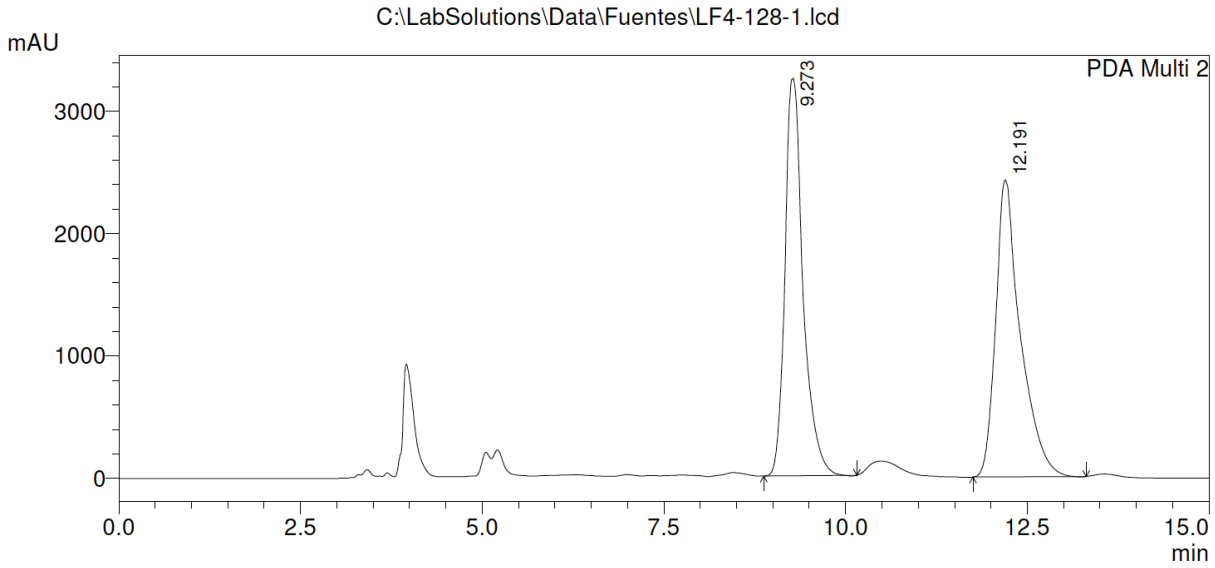
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.430	49997400	875455	96.618	97.075
2	23.223	1750061	26375	3.382	2.925
Total		51747461	901830	100.000	100.000

Racemic ***Exo*-41** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 205 nm)



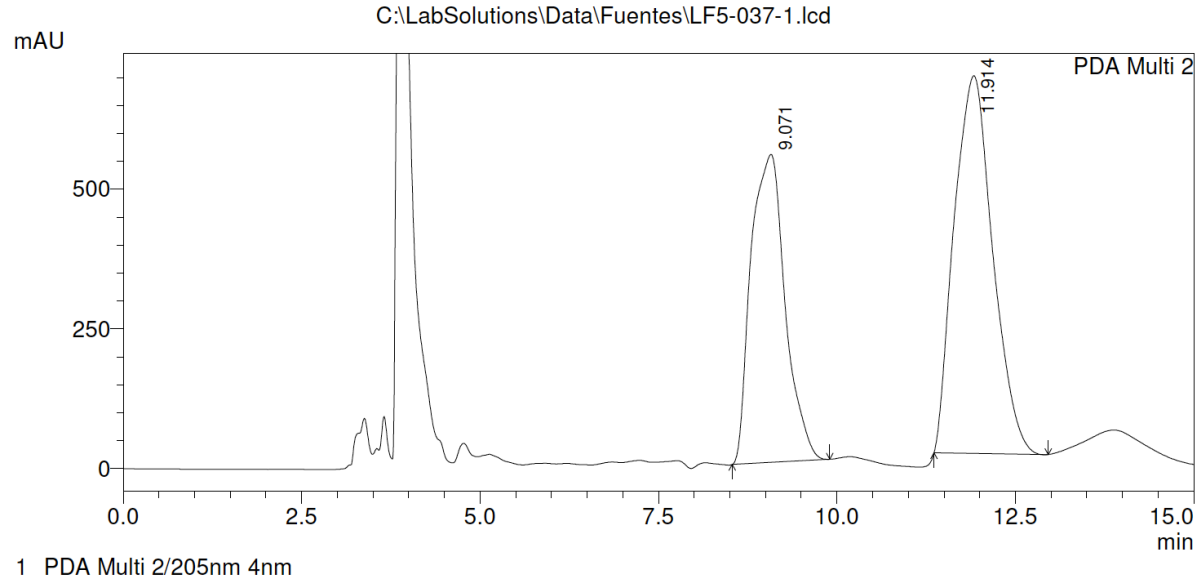
1 PDA Multi 2/205nm 4nm

PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.273	56156396	3250471	49.507	57.249
2	12.191	57274648	2427336	50.493	42.751
Total		113431044	5677806	100.000	100.000

Enantioenriched ***Exo*-41** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 205 nm)



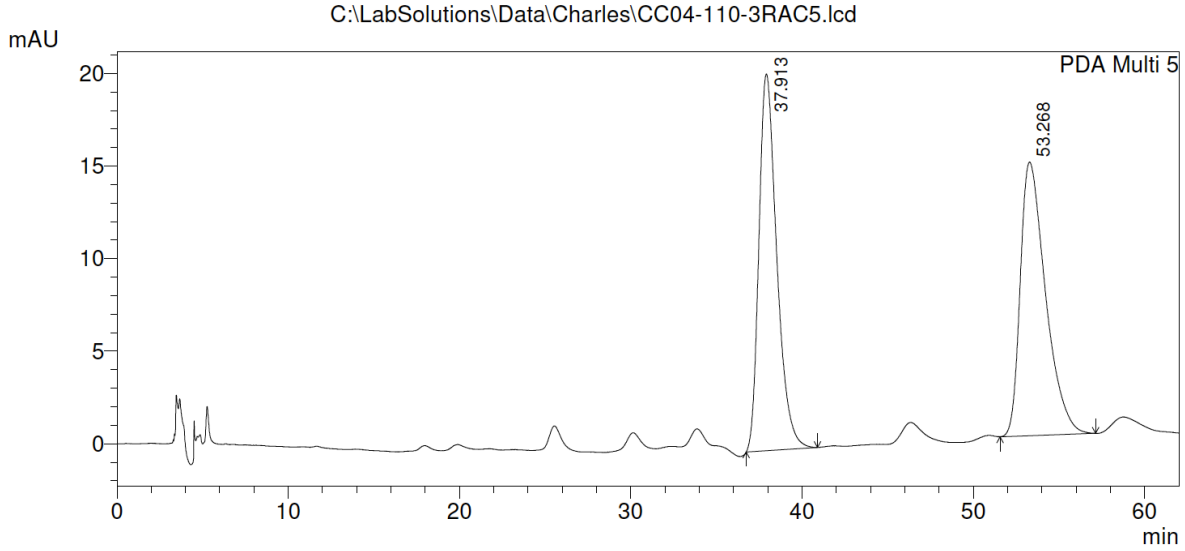
1 PDA Multi 2/205nm 4nm

PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.071	18347380	551309	41.904	44.929
2	11.914	25436502	675770	58.096	55.071
Total		43783882	1227079	100.000	100.000

Racemic ***Endo*-42** (Chiralpak IA, Hexanes/*i*PrOH 97:3, 254 nm)



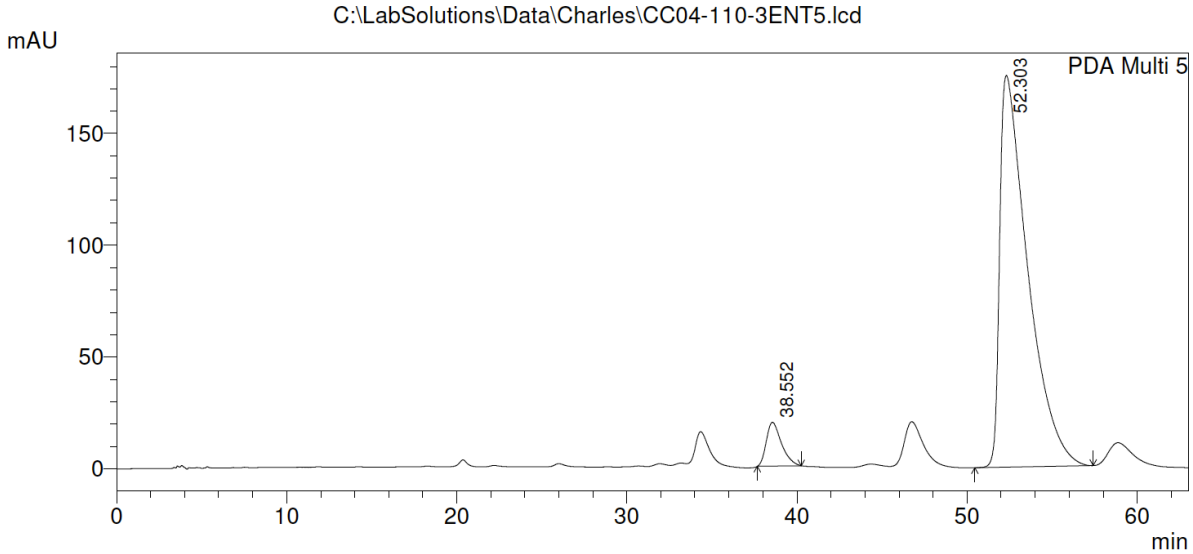
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.913	1474958	20354	49.312	57.936
2	53.268	1516091	14778	50.688	42.064
Total		2991049	35131	100.000	100.000

Enantioenriched ***Endo*-42** (Chiralpak IA, Hexanes/*i*PrOH 97:3, 254 nm)



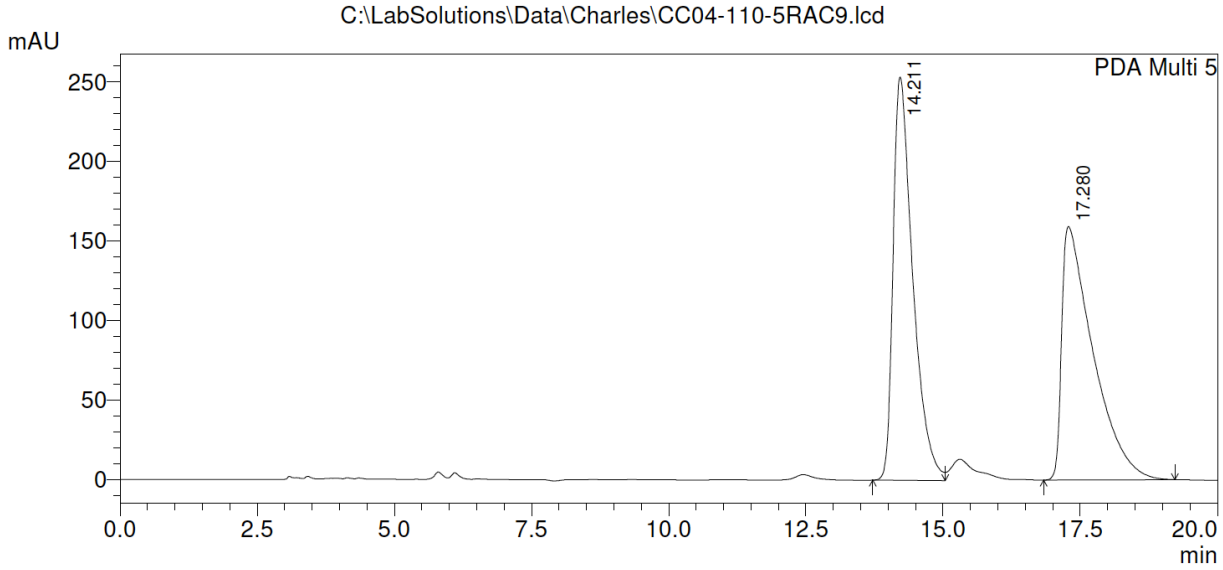
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.552	1214658	19613	5.714	10.066
2	52.303	20044748	175225	94.286	89.934
Total		21259406	194837	100.000	100.000

Racemic ***Endo*-43** (Chiralpak IA, Hexanes/*i*PrOH 88:12, 254 nm)



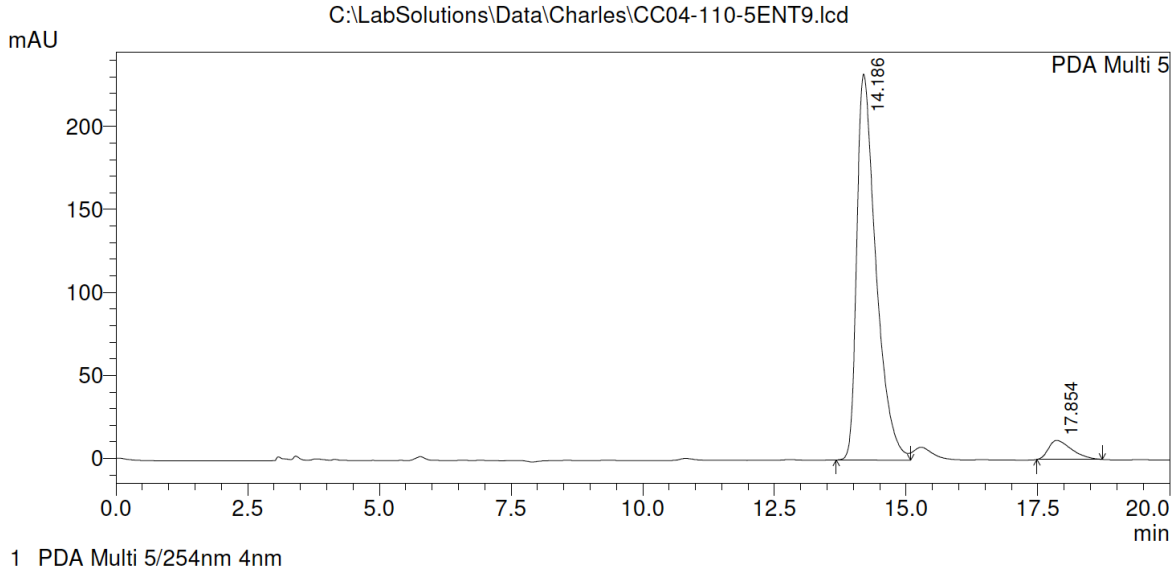
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.211	6336270	253594	50.047	61.395
2	17.280	6324427	159460	49.953	38.605
Total		12660697	413054	100.000	100.000

Enantioenriched ***Endo*-43** (Chiralpak IA, Hexanes/*i*PrOH 88:12, 254 nm)



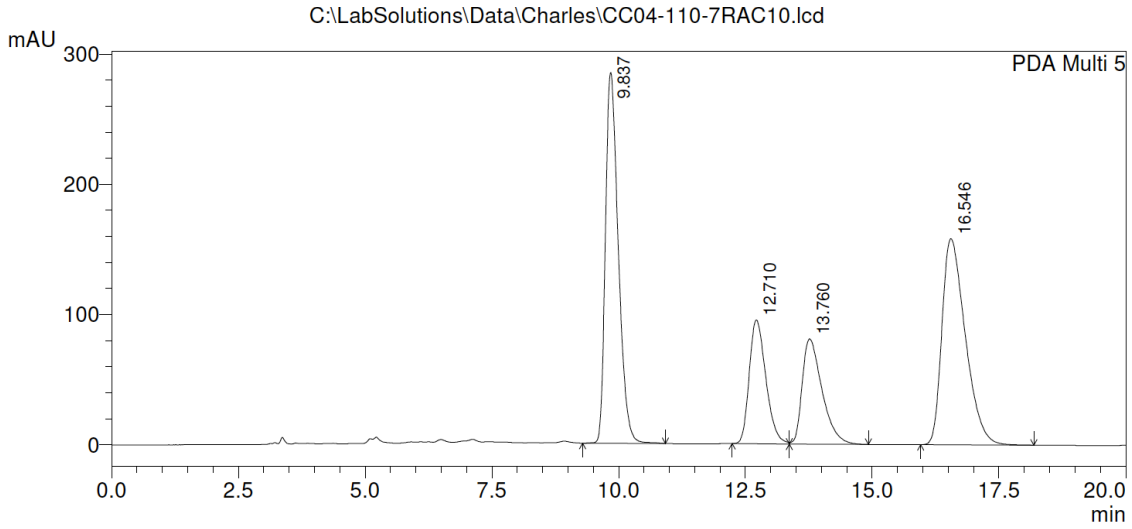
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.186	5907117	232612	94.401	95.298
2	17.854	350337	11478	5.599	4.702
Total		6257454	244090	100.000	100.000

Racemic **44** (Chiralcel OD-H, Hexanes/*i*PrOH 90:10, 254 nm)

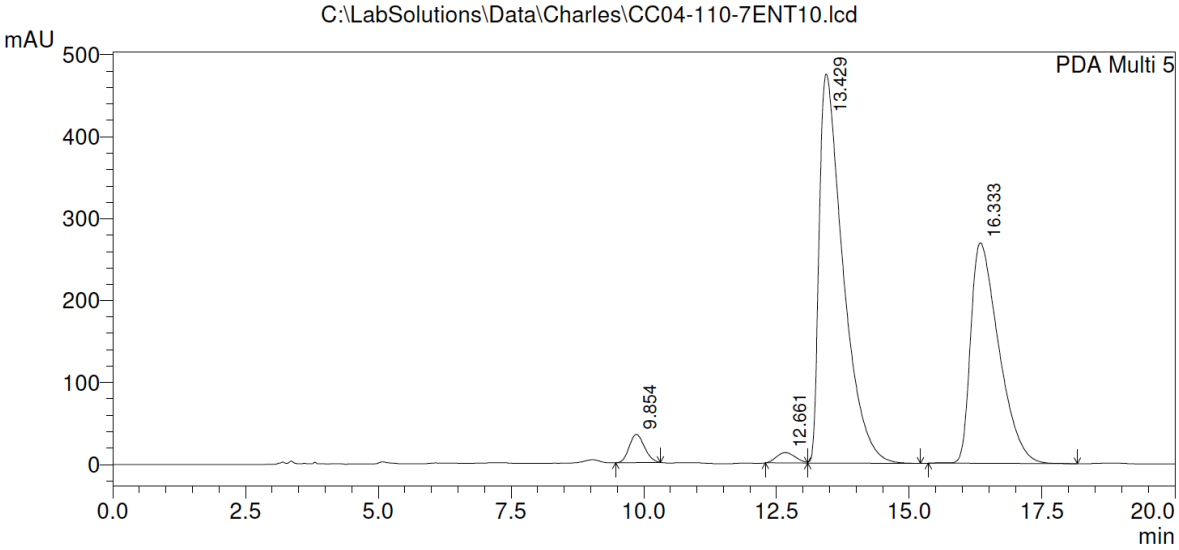


PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.837	5016277	284652	34.698	46.006
2	12.710	2167971	95064	14.996	15.364
3	13.760	2198582	80732	15.208	13.048
4	16.546	5074045	158287	35.098	25.582
Total		14456874	618734	100.000	100.000

Enantioenriched **44** (Chiralcel OD-H, Hexanes/*i*PrOH 90:10, 254 nm)

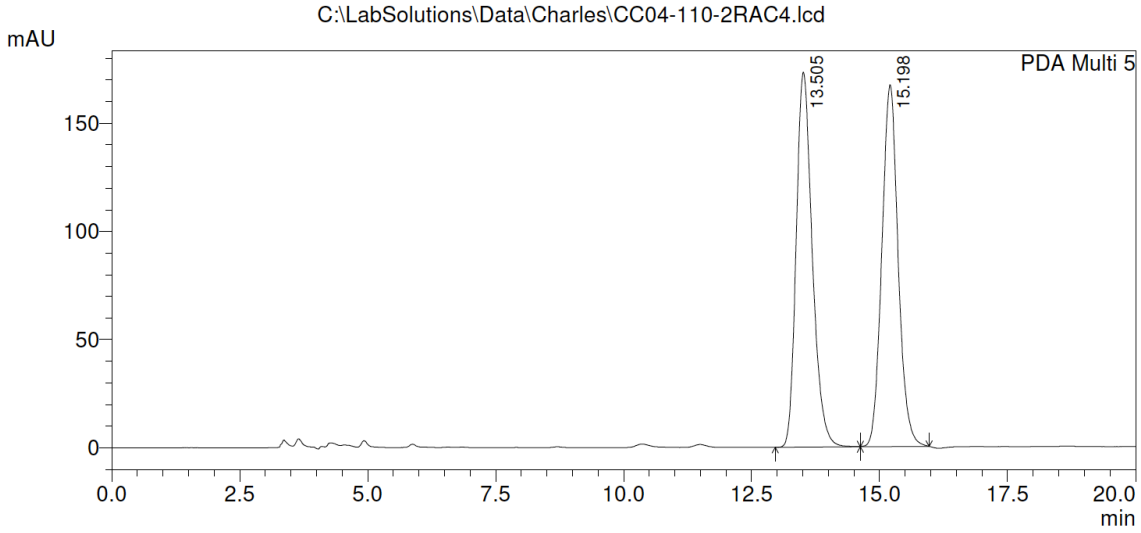


PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.854	692226	34429	2.691	4.354
2	12.661	310365	12596	1.206	1.593
3	13.429	14823458	474667	57.616	60.025
4	16.333	9902165	269091	38.488	34.028
Total		25728215	790783	100.000	100.000

Racemic ***Endo*-45** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



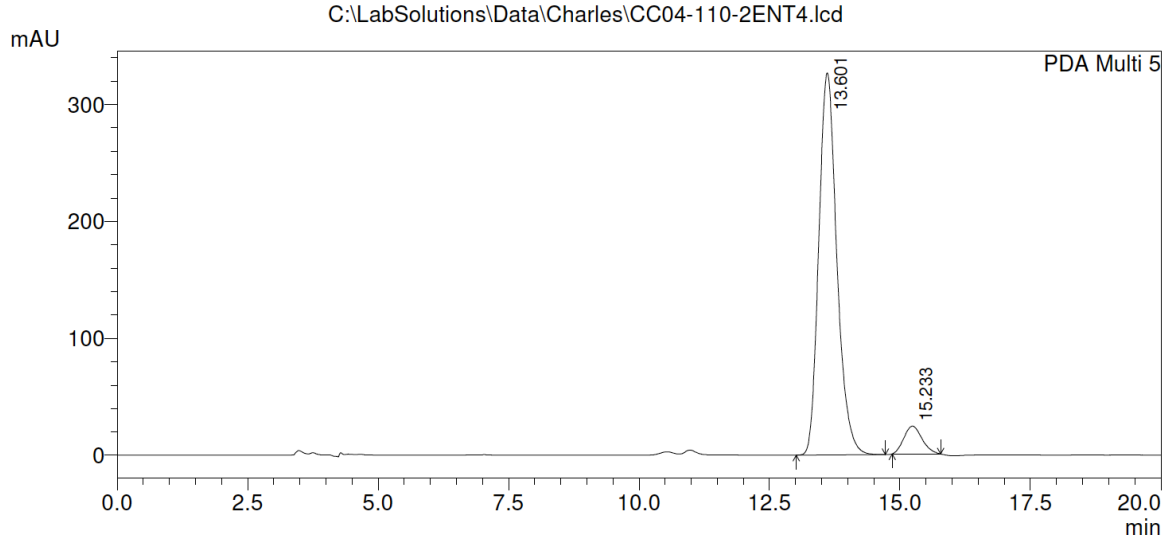
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.505	3789793	173302	50.545	50.883
2	15.198	3708070	167286	49.455	49.117
Total		7497863	340588	100.000	100.000

Enantioenriched ***Endo*-45** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



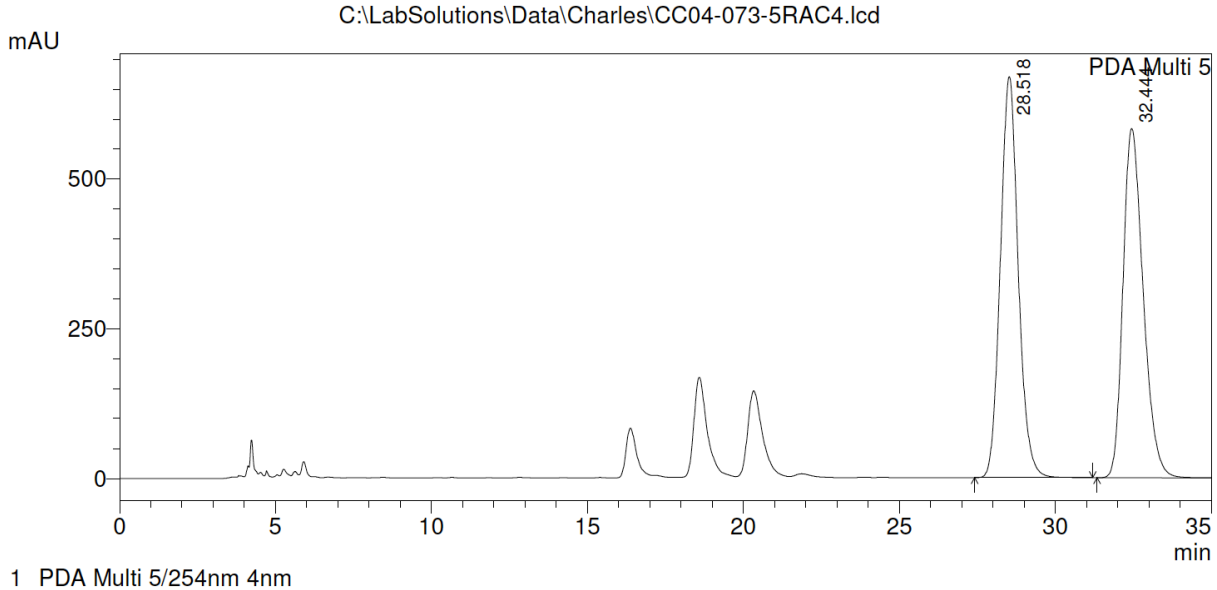
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.601	7865847	326769	93.176	93.221
2	15.233	576074	23764	6.824	6.779
Total		8441921	350533	100.000	100.000

Racemic ***Endo*-46** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



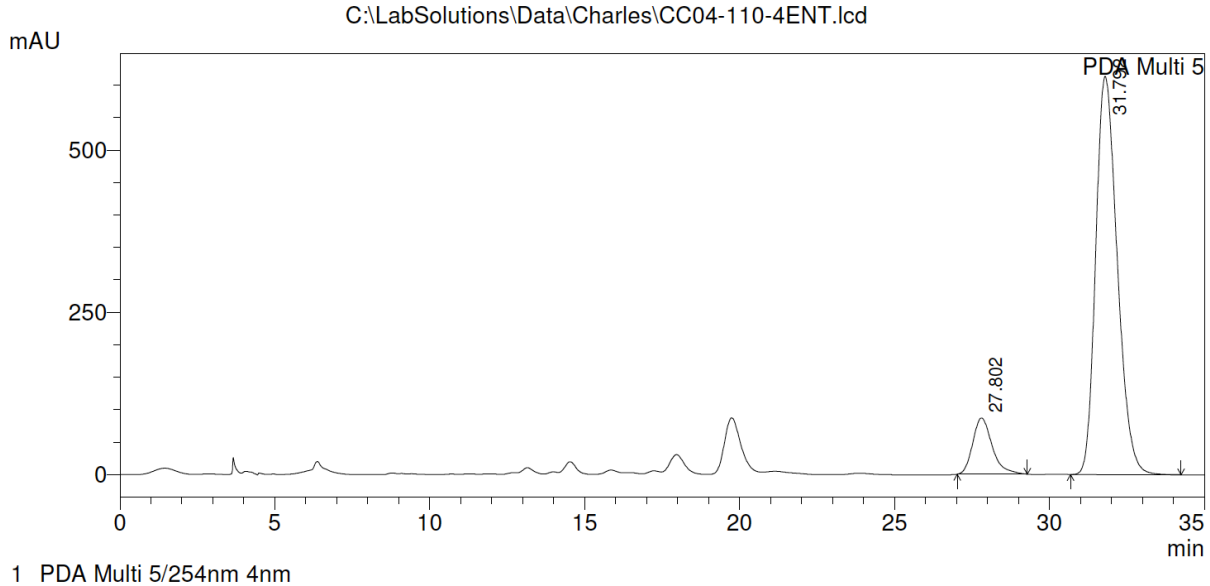
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.518	26744807	669883	50.416	53.447
2	32.444	26303396	583482	49.584	46.553
Total		53048203	1253365	100.000	100.000

Enantioenriched ***Endo*-46** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



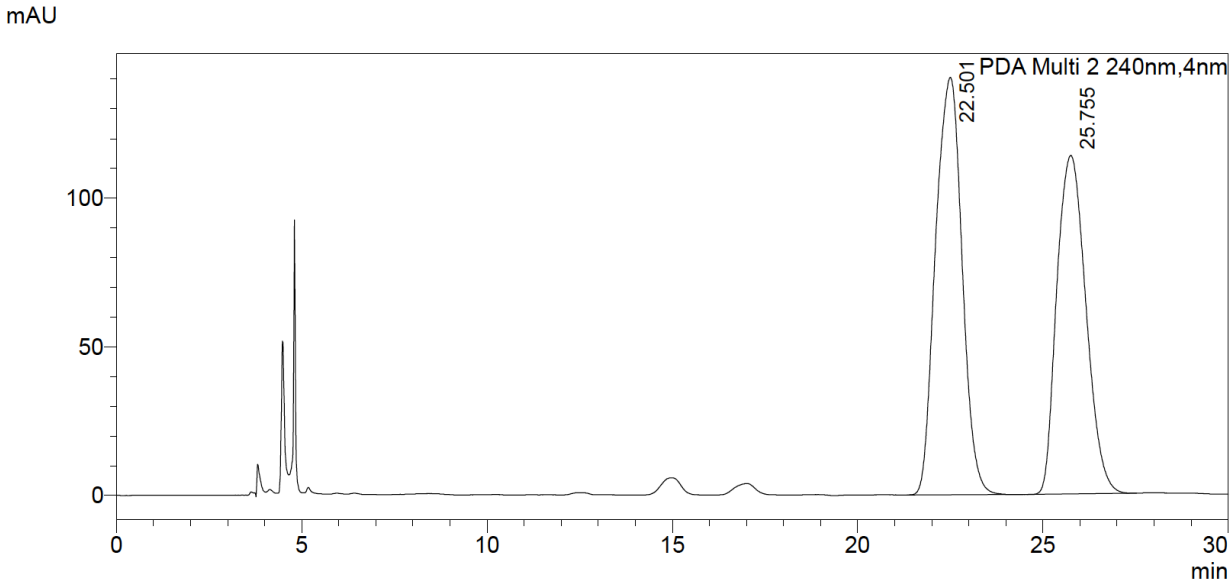
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.802	3784088	86527	11.321	12.363
2	31.792	29642661	613355	88.679	87.637
Total		33426749	699882	100.000	100.000

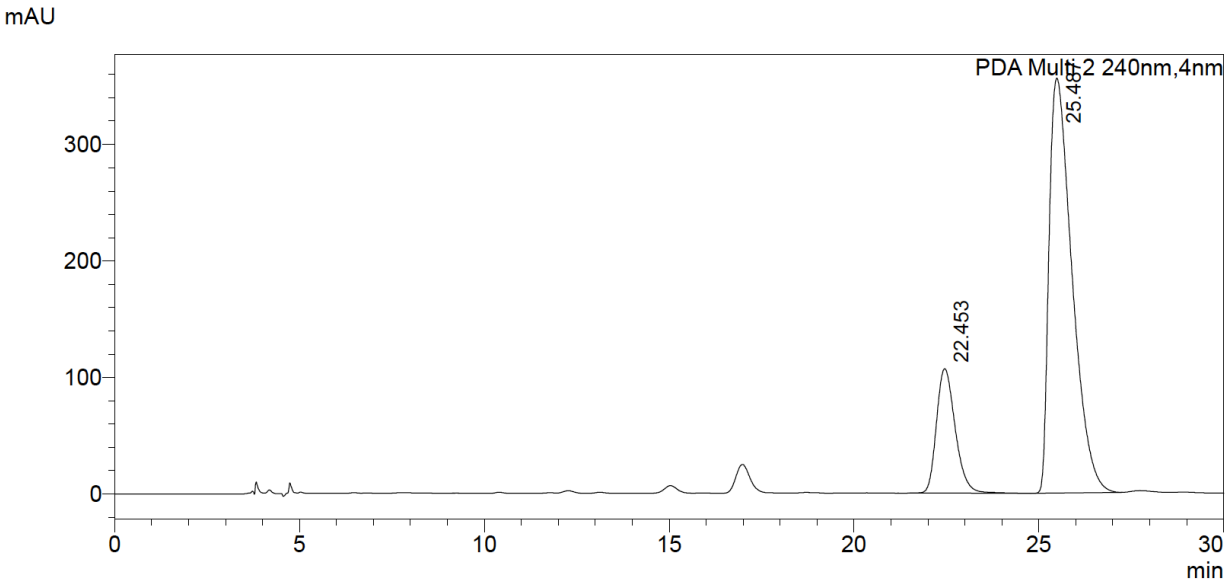
Racemic **Endo-47** (Chiralpak AD-H, Hexanes/*i*PrOH, 95:5, 240 nm)



PDA Ch2 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.501	6987684	140380	52.893	55.215
2	25.755	6223383	113862	47.107	44.785
Total		13211066	254242	100.000	100.000

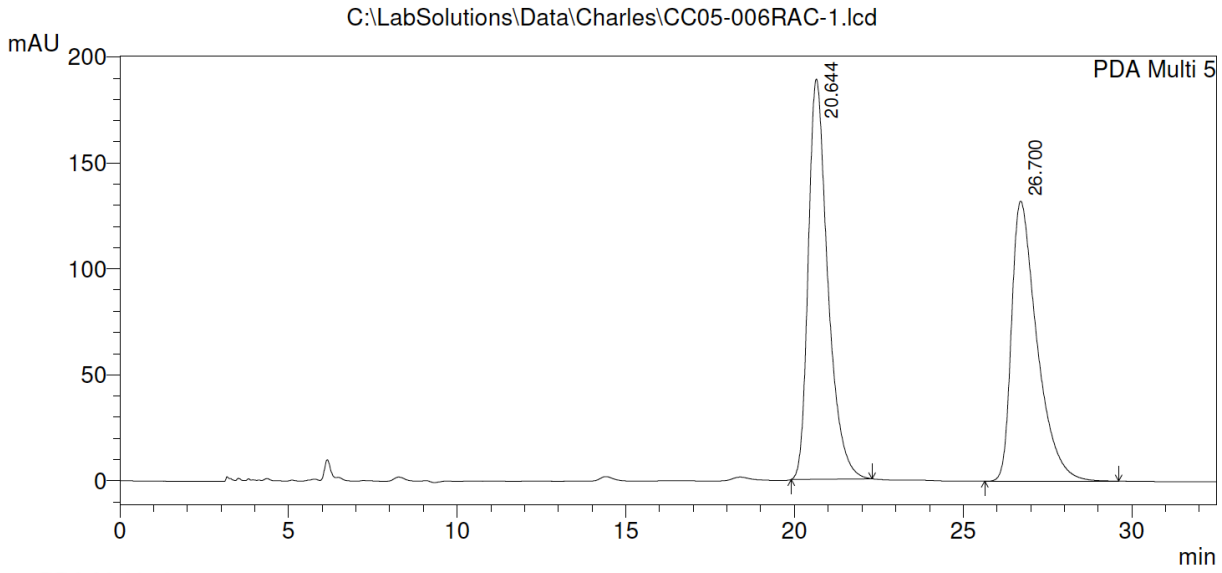
Enantioenriched **Endo-47** (Chiralpak AD-H, Hexanes/*i*PrOH, 95:5, 240 nm)



PDA Ch2 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.453	3777674	106893	19.710	23.087
2	25.487	15388599	356108	80.290	76.913
Total		19166274	463001	100.000	100.000

Racemic ***Endo*-51** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



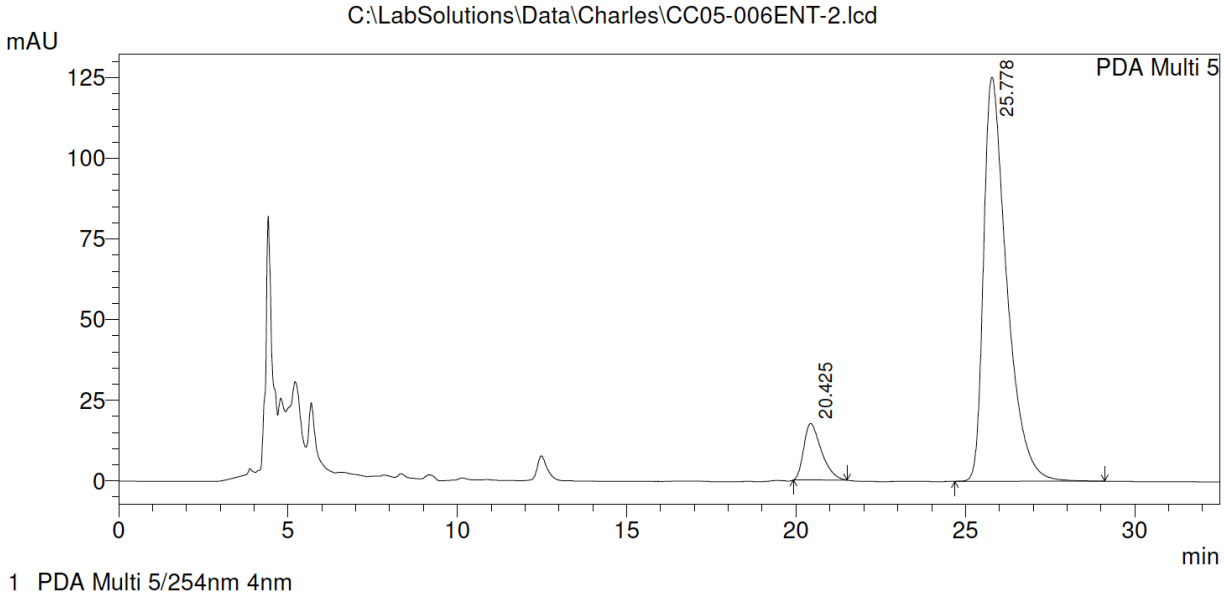
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.644	7602453	188892	52.282	58.832
2	26.700	6938674	132177	47.718	41.168
Total		14541128	321069	100.000	100.000

Enantioenriched ***Endo*-51** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



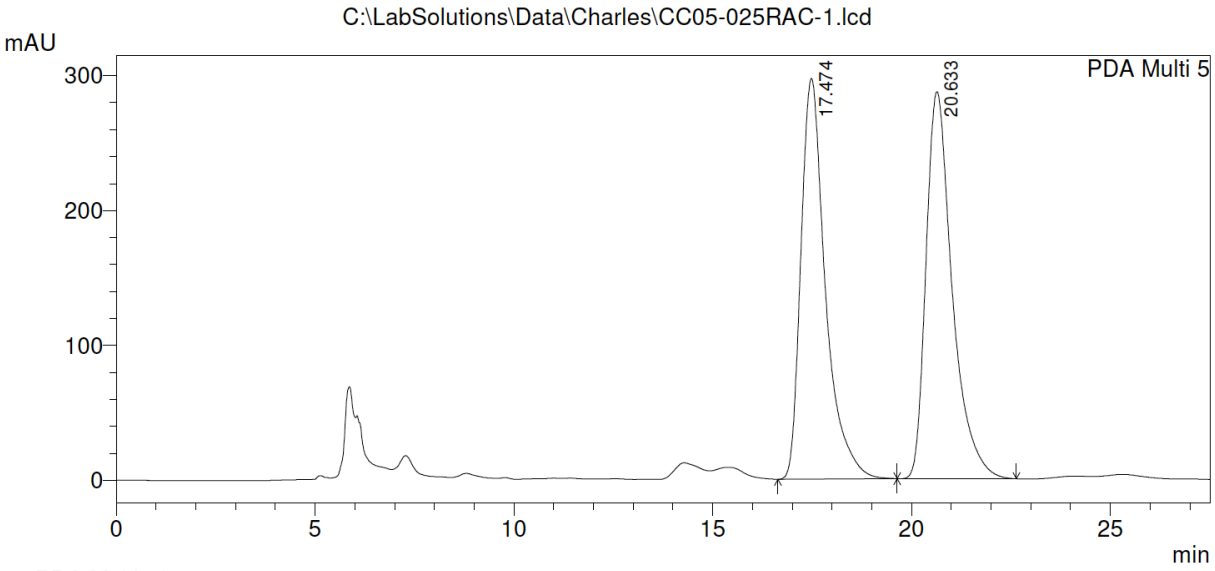
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.425	632826	17483	9.598	12.256
2	25.778	5960170	125166	90.402	87.744
Total		6592996	142649	100.000	100.000

Racemic ***Endo*-52** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



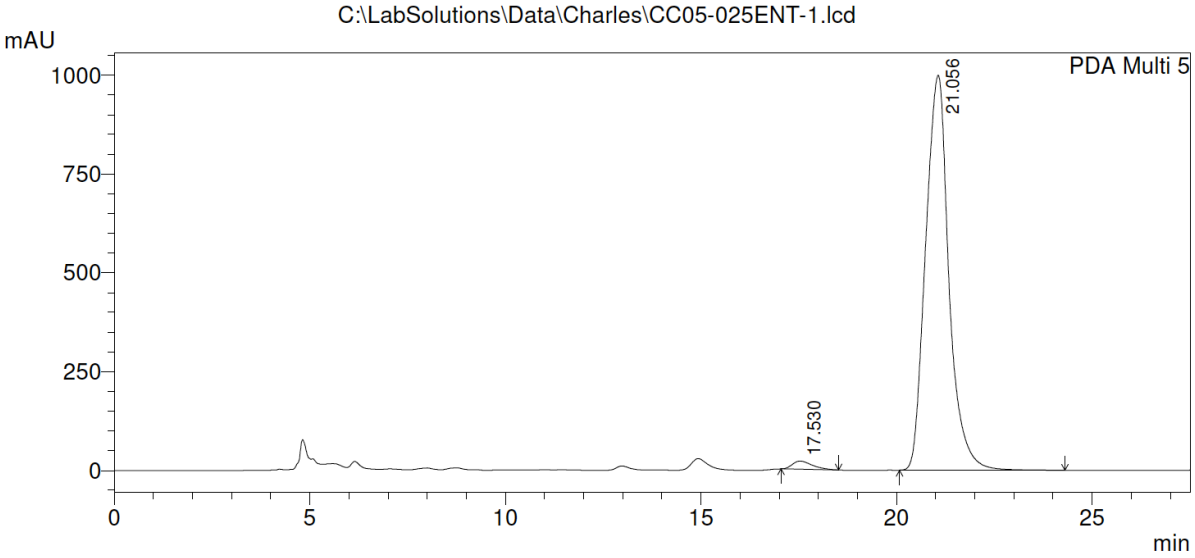
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.474	12716112	297063	49.157	50.868
2	20.633	13152424	286920	50.843	49.132
Total		25868536	583983	100.000	100.000

Enantioenriched ***Endo*-52** (Chiralpak IA, Hexanes/*i*PrOH 90:10, 254 nm)



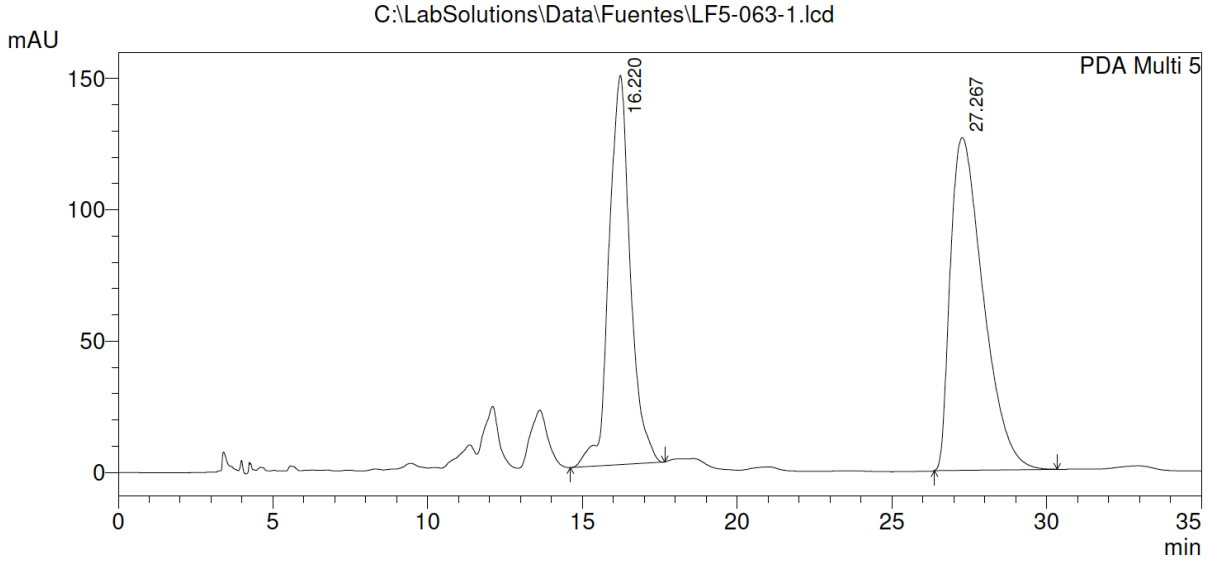
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.530	735208	20670	1.747	2.028
2	21.056	41337255	998760	98.253	97.972
Total		42072463	1019430	100.000	100.000

Racemic **54** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



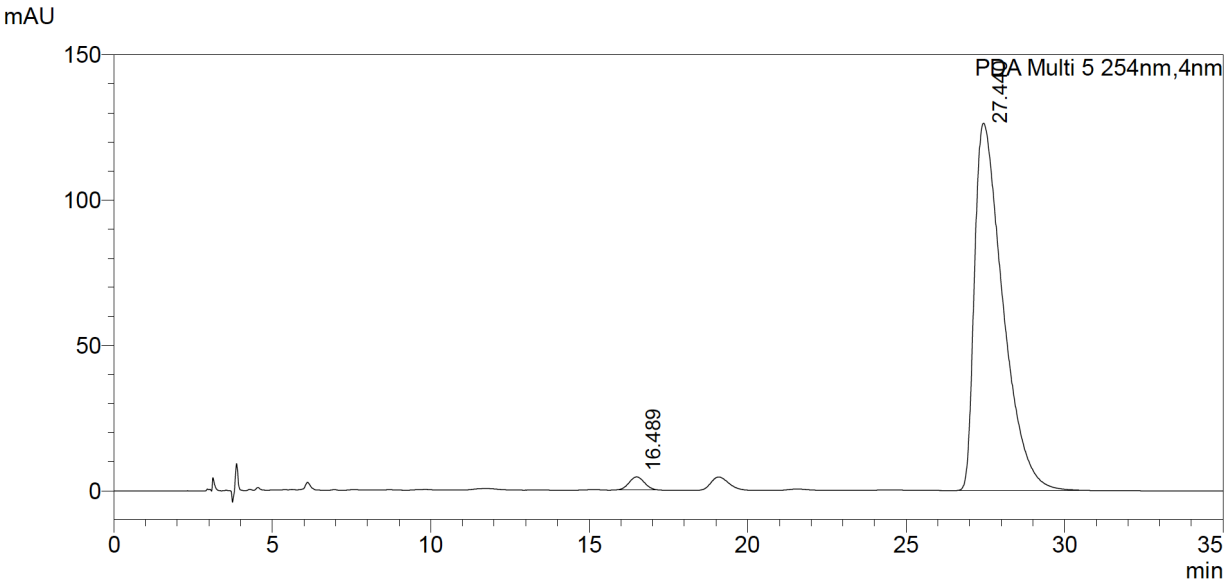
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.220	7122348	148356	43.247	53.919
2	27.267	9346824	126792	56.753	46.081
Total		16469173	275149	100.000	100.000

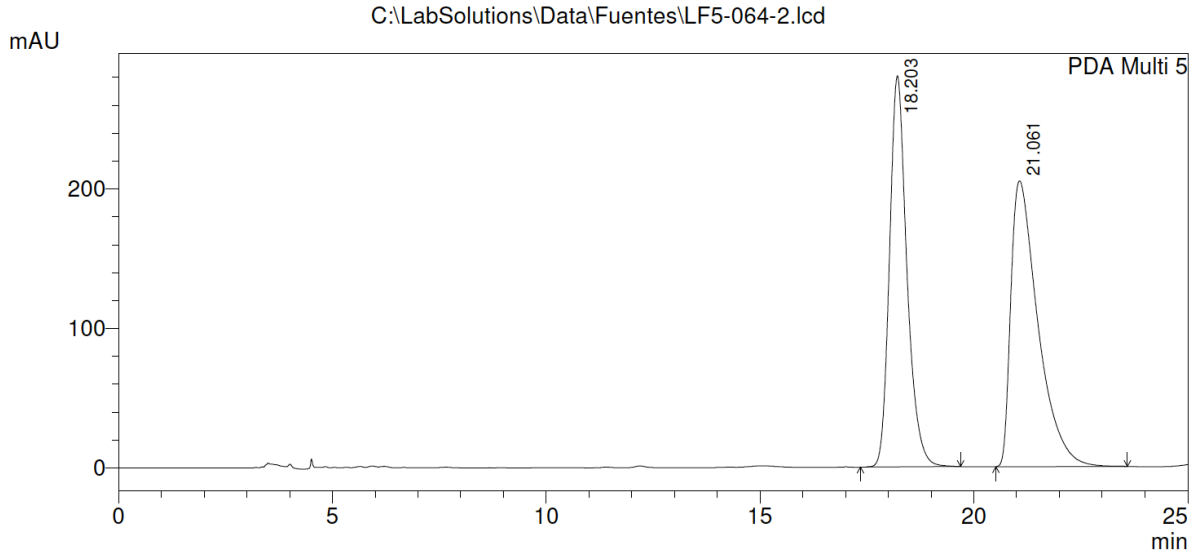
Enantioenriched **54** (Chiralpak AD-H, Hexanes/*i*PrOH 95:5, 254 nm)



PDA Ch5 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.489	154791	4524	1.932	3.456
2	27.440	7857043	126386	98.068	96.544
Total		8011834	130910	100.000	100.000

Racemic **55** (Chiralpak AD-H, Hexanes/*i*PrOH 97:3, 254 nm)



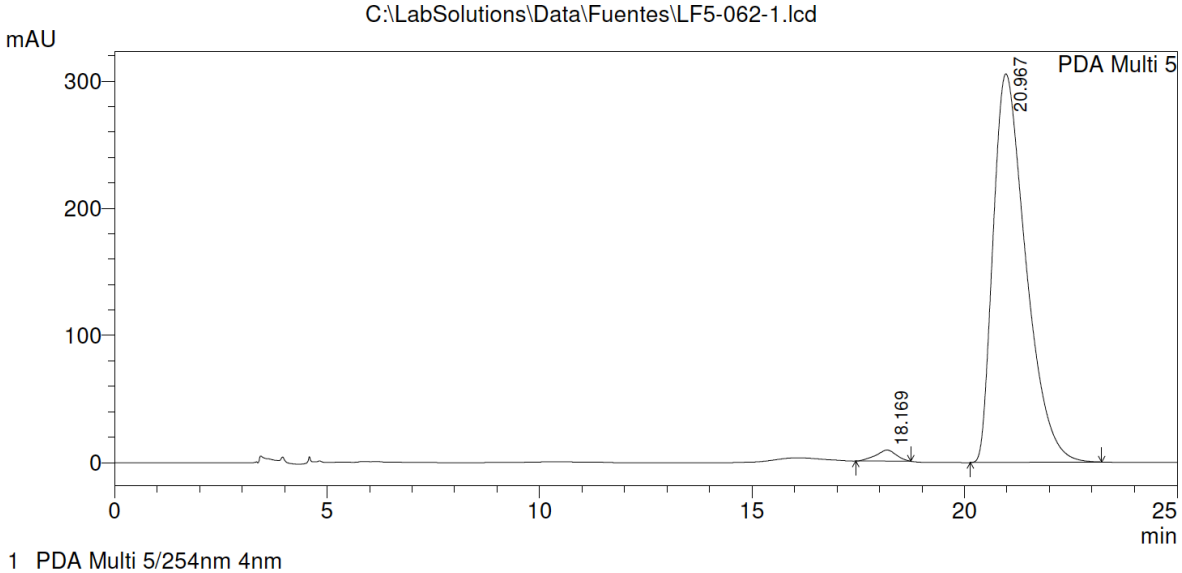
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.203	7939134	280392	46.827	57.785
2	21.061	9014991	204843	53.173	42.215
Total		16954124	485235	100.000	100.000

Enantioenriched **55** (Chiralpak AD-H, Hexanes/*i*PrOH 97:3, 254 nm)



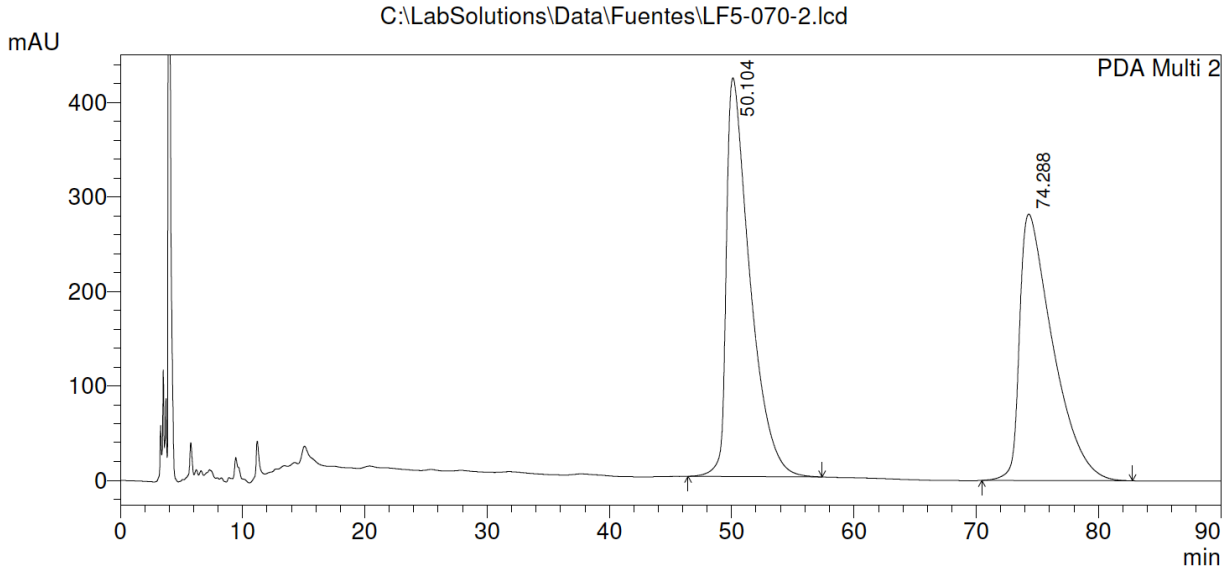
1 PDA Multi 5/254nm 4nm

PeakTable

PDA Ch5 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.169	293398	8703	1.768	2.768
2	20.967	16301701	305727	98.232	97.232
Total		16595098	314430	100.000	100.000

Racemic **57** (Chiralcel OD-H, Hexanes/*i*PrOH 90:10, 205 nm)



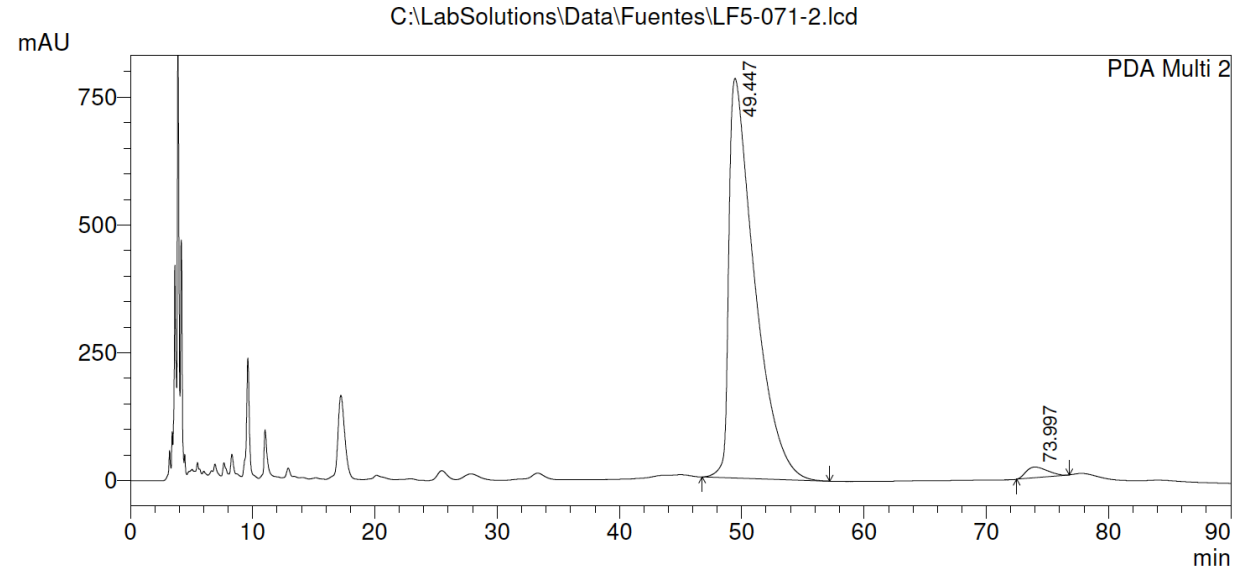
1 PDA Multi 2/205nm 4nm

PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.104	56832069	422211	51.590	59.940
2	74.288	53329972	282181	48.410	40.060
Total		110162041	704392	100.000	100.000

Enantioenriched **57** (Chiralcel OD-H, Hexanes/*i*PrOH 90:10, 205 nm)



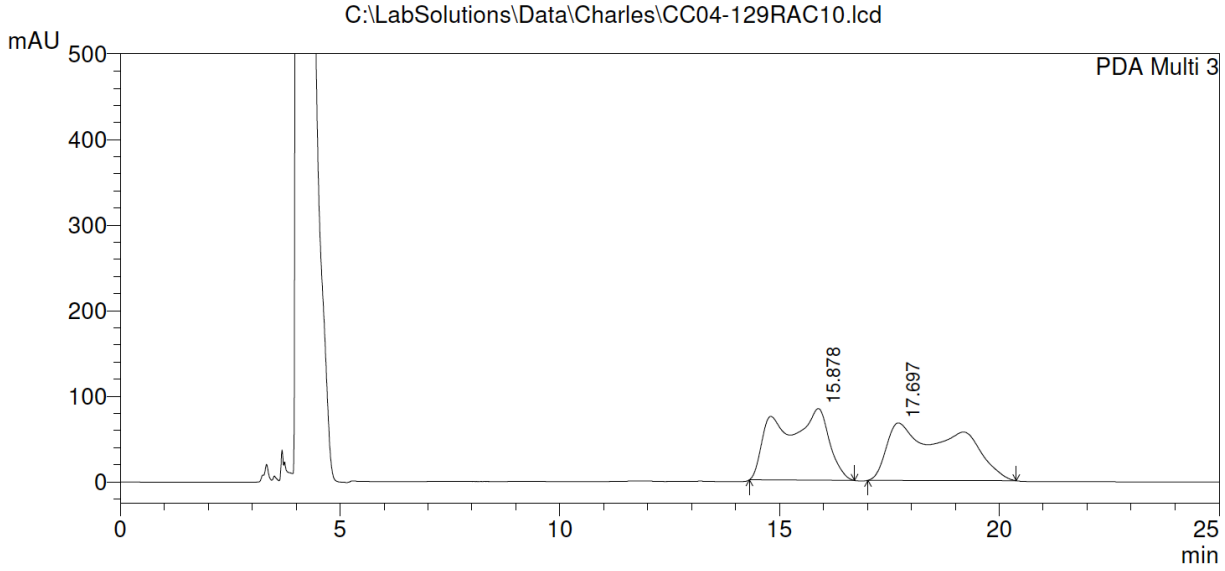
1 PDA Multi 2/205nm 4nm

PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.447	113870491	782008	97.835	97.402
2	73.997	2520135	20859	2.165	2.598
Total		116390626	802867	100.000	100.000

Racemic **58** (Chiralcel OJ-H, Hexanes/*i*PrOH 99:1, 215 nm)



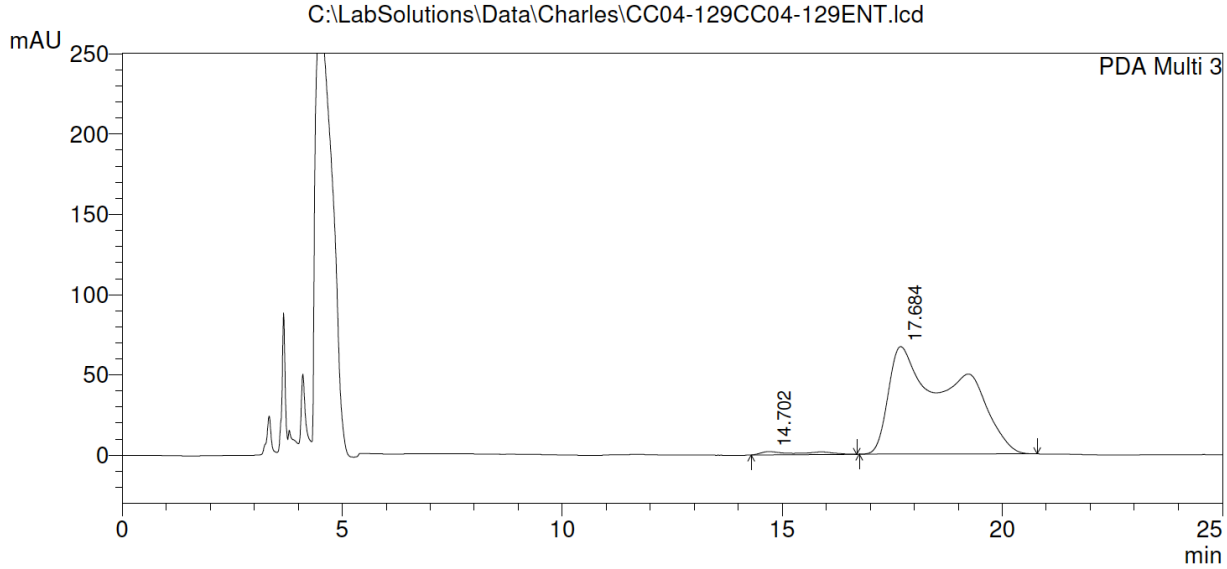
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.878	6678515	83808	47.405	55.533
2	17.697	7409694	67108	52.595	44.467
Total		14088209	150917	100.000	100.000

Enantioenriched **58** (Chiralcel OJ-H, Hexanes/*i*PrOH 99:1, 215 nm)



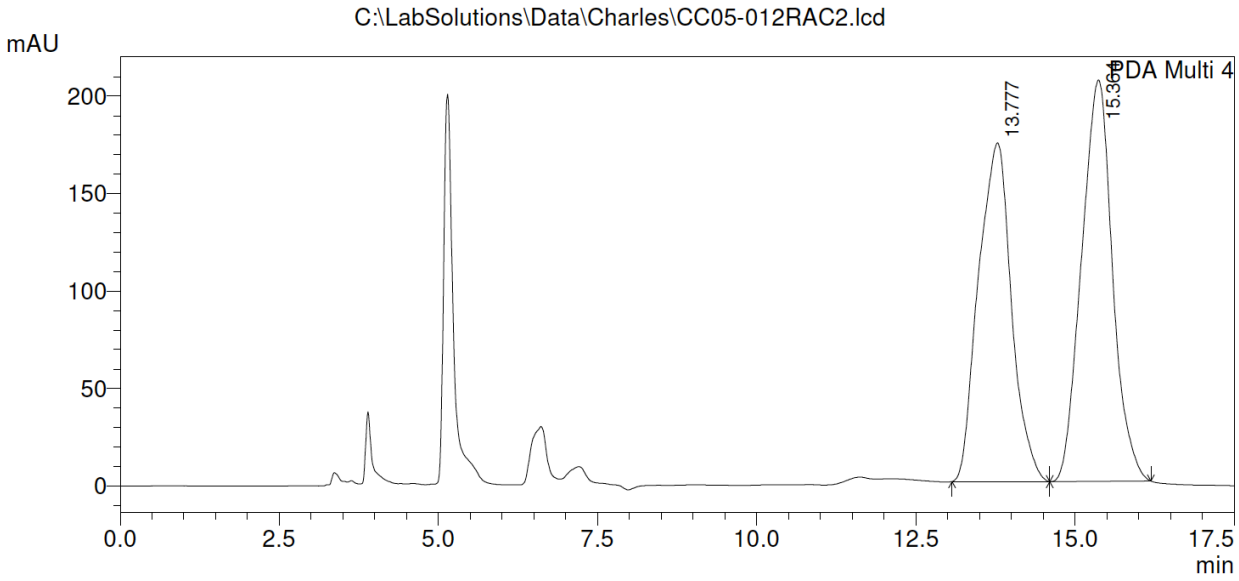
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.702	144308	2041	1.983	2.959
2	17.684	7134381	66956	98.017	97.041
Total		7278689	68998	100.000	100.000

Racemic **60** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 240 nm)



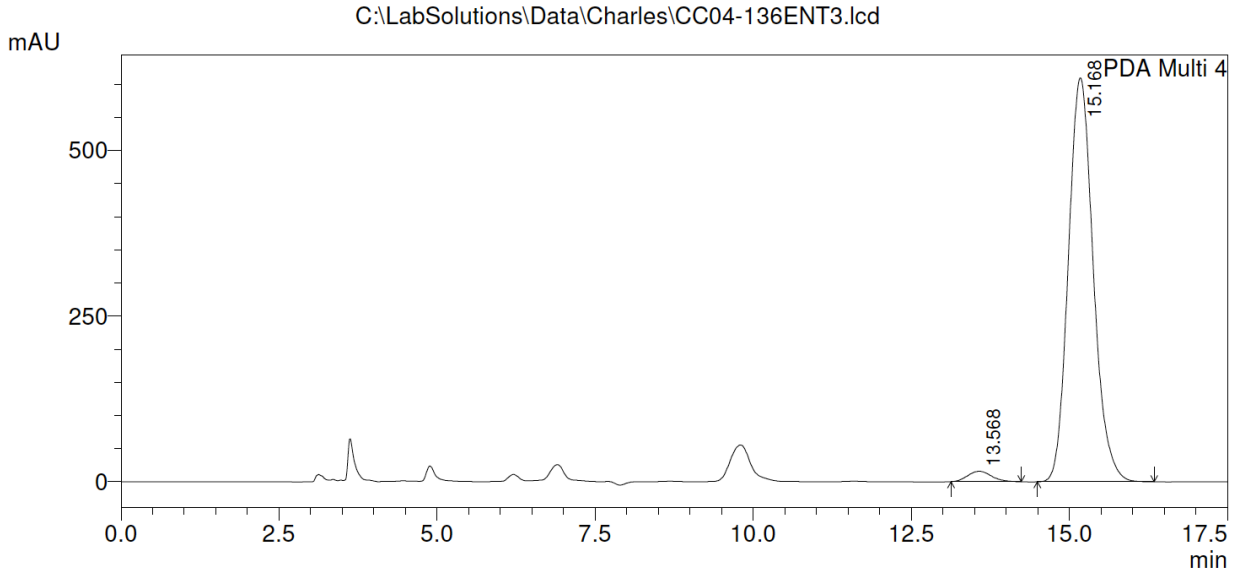
1 PDA Multi 4/240nm 1nm

PeakTable

PDA Ch4 240nm 1nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.777	6255295	173727	47.330	45.769
2	15.364	6961091	205849	52.670	54.231
Total		13216387	379575	100.000	100.000

Enantioenriched **60** (Chiralpak AD-H, Hexanes/*i*PrOH 90:10, 240 nm)



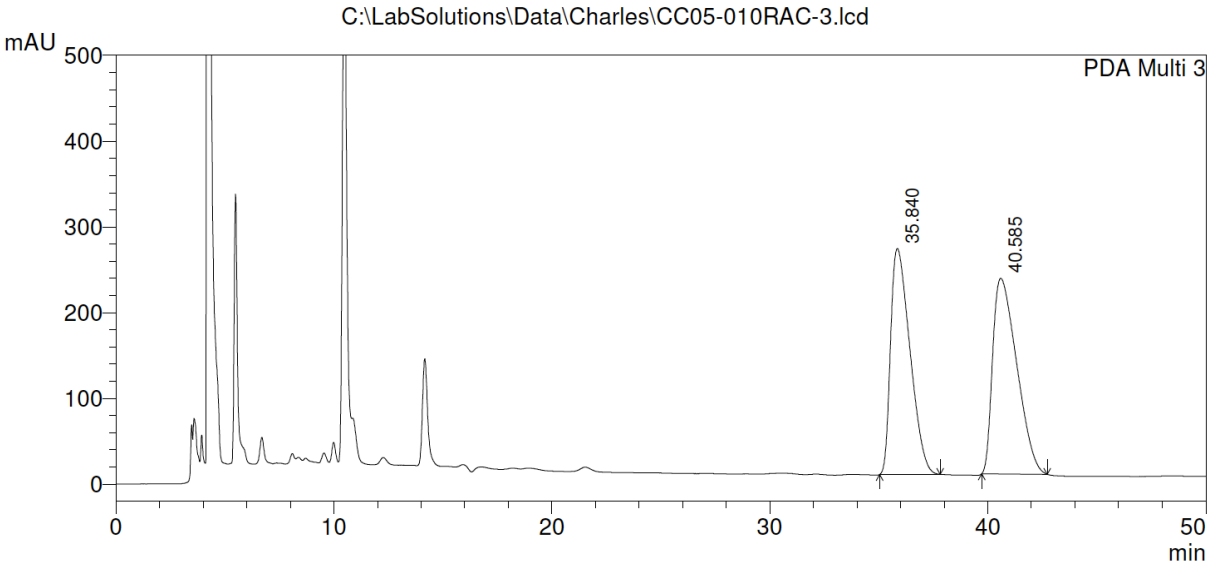
1 PDA Multi 4/240nm 1nm

PeakTable

PDA Ch4 240nm 1nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.568	413230	15703	2.415	2.513
2	15.168	16698964	609100	97.585	97.487
Total		17112195	624803	100.000	100.000

Racemic **61** (Chiralpak AS-H, Hexanes/*i*PrOH 90:10, 215 nm)



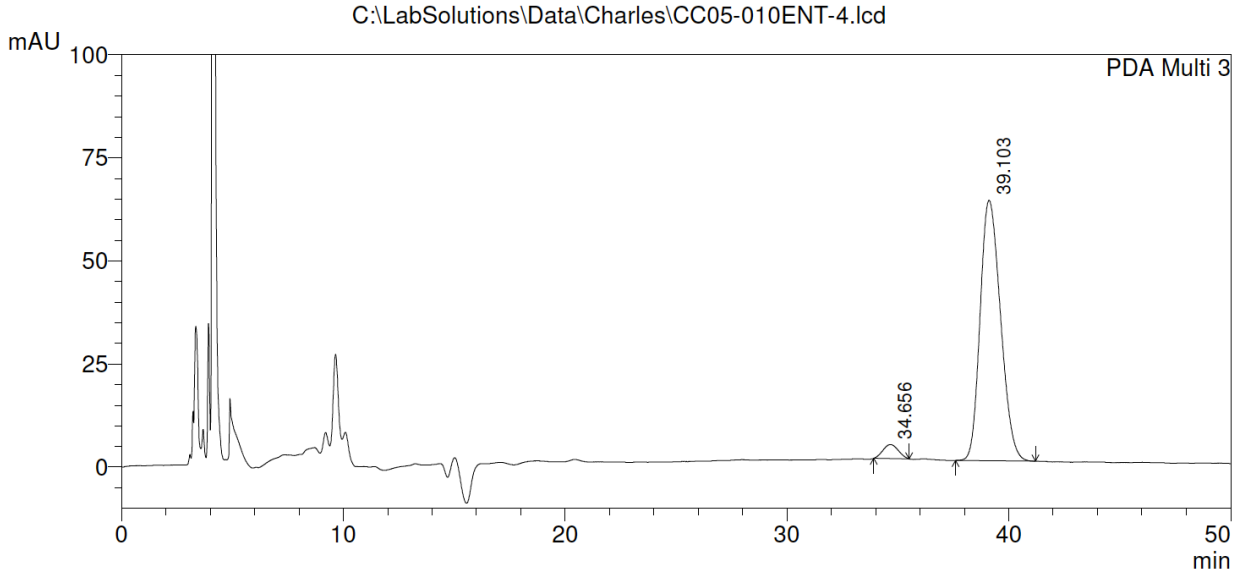
1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.840	16239806	263521	48.142	53.591
2	40.585	17493105	228210	51.858	46.409
Total		33732910	491730	100.000	100.000

Enantioenriched **61** (Chiralpak AS-H, Hexanes/*i*PrOH 90:10, 215 nm)



1 PDA Multi 3/215nm 4nm

PeakTable

PDA Ch3 215nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.656	163203	3402	3.882	5.108
2	39.103	4040418	63202	96.118	94.892
Total		4203621	66605	100.000	100.000

J. X-Ray Crystallographic Data

(Note: All crystal structures are of the corresponding Wittig products)

General information: The diffraction data were measured at 100 K on a Bruker D8 VENTURE diffractometer equipped with a microfocus Mo-target X-ray tube (λ = 0.71073 Å) and PHOTON 100 CMOS detector. Data were collected using ϕ and ω scans to survey a hemisphere of reciprocal space. Data reduction and integration were performed with the Bruker APEX3 software package (Bruker AXS, version 2017.3-0, 2018). Data were scaled and corrected for absorption effects using the multi-scan procedure as implemented in SADABS (Bruker AXS, version 2014/5, Krause, Herbst-Irmer, Sheldrick & Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10). The structure was solved by SHELXT (Version 2014/5: Sheldrick, G. M. *Acta Crystallogr*. **2015**, *A71*, 3-8) and refined by a full-matrix least-squares procedure using OLEX2 (O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. J. Appl. Crystallogr. **2009**, *42*, 339-341) (XL refinement program version 2018/1, *Sheldrick, G. M. Acta Crystallogr.* **2015**, *C71*, 3-8). Crystallographic data and details of the data collection and structure refinement are listed in Table 1.

Specific details for structure refinement: All atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions for structure factor calculations. All structures are drawn with thermal ellipsoids at 50% probability.

Crystal Structure of *Endo*-24

Table S3 Crystal data and structure refinement for cu_0682_Cole_AM_0m.

Identification code	cu_0682_Cole_AM_0m
Empirical formula	$C_{17}H_{20}O_6$
Formula weight	320.33
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.0910(4)
b/Å	16.2621(9)
c/Å	13.2704(7)
α/°	90
β/°	92.494(2)
γ/°	90
Volume/Å^3	1528.82(15)
Z	4
ρ_{calc}g/cm^3	1.392
μ/mm^{-1}	0.881
F(000)	680.0
Crystal size/mm^3	0.38 × 0.31 × 0.28
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.666 to 145.374
Index ranges	$-8 \le h \le 8$, $-20 \le k \le 20$, $-16 \le l \le 16$
Reflections collected	25135
Independent reflections	6029 [R_{int} = 0.0301, R_{sigma} = 0.0249]

Data/restraints/parameters	6029/1/419
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.0280, wR_2 = 0.0709
Largest diff. peak/hole / e Å^{-3}	0.20/-0.19
Flack parameter	-0.01(4)
Hooft parameter	0.01(3)

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

Goodness-of-fit = $[\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S1

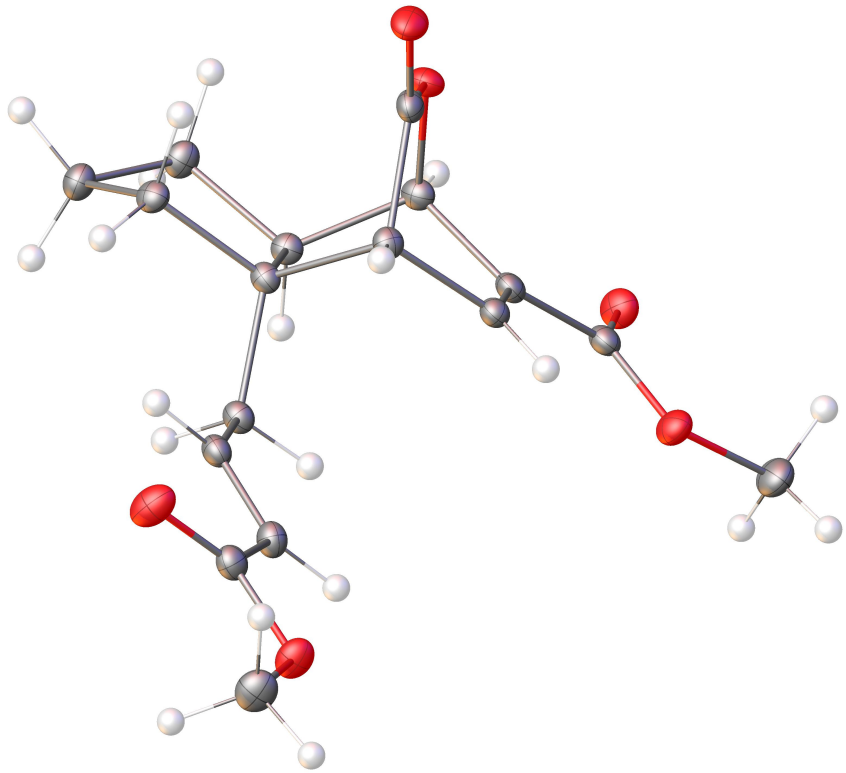


Table S4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_0682_Cole_AM_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4748.8(19)	824.5(9)	12088.9(9)	21.4(3)
O2	5961.9(19)	1674.8(9)	13287.2(10)	22.5(3)
O3	3320.0(17)	3568.7(8)	11883.7(9)	17.9(3)
O4	1025.4(18)	3822.8(9)	10737.3(10)	24.0(3)
O5	4373(2)	2490.8(9)	6480.5(10)	25.2(3)

O6	4788(2)	1131.5(9)	6695.0(11)	24.6(3)
C1	5084(3)	144.0(12)	12776.3(15)	26.3(4)
C2	5229(2)	1565.9(12)	12459.5(13)	16.0(3)
C3	4739(2)	2233.4(11)	11738.9(13)	16.1(3)
C4	5115(2)	3118.5(11)	12008.5(13)	16.1(3)
C5	2491(2)	3480.3(12)	10953.5(14)	17.0(3)
C6	3926(2)	2139.8(12)	10821.5(13)	16.7(3)
C7	3617(2)	2941.7(12)	10266.0(13)	16.4(3)
C8	5603(2)	3362.5(11)	10169.6(13)	15.1(3)
C9	6476(2)	3491.6(11)	11262.9(13)	15.5(3)
C10	6739(3)	4428.8(11)	11399.2(14)	19.0(4)
C11	5393(3)	4835.4(12)	10609.6(14)	21.2(4)
C12	5400(3)	4234.3(11)	9714.6(13)	18.6(4)
C13	6860(2)	2811.5(12)	9532.1(13)	17.8(3)
C14	6048(2)	2692.0(12)	8479.3(13)	18.5(4)
C15	5734(3)	1972.0(12)	8038.9(14)	19.4(4)
C16	4899(3)	1918.4(12)	6995.7(14)	18.9(4)
C17	3969(3)	1008.3(13)	5689.7(15)	28.0(4)
O7	-123.4(19)	6729.8(9)	2601.1(10)	21.6(3)
O8	-843.4(19)	7957.2(9)	1903.7(9)	22.8(3)
O9	2082.2(17)	9128.5(8)	4098.0(10)	18.3(3)
O10	4375.3(18)	8933.1(9)	5268.2(11)	22.6(3)
O11	-95(2)	5393.7(9)	7976.0(10)	22.3(3)
O12	457(2)	6620.1(9)	8702.2(10)	27.1(3)
C18	-597(3)	6344.5(13)	1639.3(15)	25.9(4)
C19	-271(2)	7554.0(12)	2616.2(13)	17.0(4)
C20	372(2)	7901.9(12)	3596.1(13)	16.1(3)
C21	197(2)	8812.9(11)	3783.0(13)	16.1(3)
C22	-1119(2)	8945.7(11)	4655.0(13)	15.1(3)
C23	-242(2)	8483.7(11)	5603.9(12)	14.2(3)
C24	1621(2)	8044.2(11)	5281.3(13)	15.4(3)
C25	2872(2)	8724.6(11)	4901.6(13)	16.5(3)
C26	1133(2)	7498.9(11)	4388.4(13)	15.3(3)
C27	-1336(3)	9853.7(12)	4971.2(14)	19.6(4)
C28	-1375(3)	9821.7(12)	6125.6(14)	19.4(4)
C29	112(2)	9165.9(11)	6398.9(13)	16.9(3)
C30	-1622(2)	7826.0(11)	5971.6(12)	15.8(3)
C31	-869(2)	7365.7(12)	6880.2(13)	16.5(3)
C32	-762(2)	6559.8(12)	6992.5(13)	18.1(4)
C33	-62(2)	6221.1(12)	7978.3(14)	17.9(4)
C34	478(3)	5015.9(13)	8930.1(15)	25.5(4)

Table S5 Anisotropic Displacement Parameters ($Å^2×10^3$) for cu_0682_Cole_AM_0m. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	31.3(7)	17.8(6)	15.0(6)	1.7(5)	-1.1(5)	-3.8(6)
O2	26.6(7)	22.5(7)	17.7(6)	1.1(5)	-5.2(5)	-3.4(6)
O3	16.4(6)	22.1(7)	15.5(6)	-0.8(5)	2.7(5)	2.2(5)
O4	16.5(6)	32.4(8)	23.1(7)	2.5(6)	2.0(5)	5.8(5)
O5	33.4(7)	22.2(7)	19.5(6)	0.3(6)	-2.4(6)	3.2(6)
O6	32.0(7)	19.6(7)	21.8(7)	-2.2(6)	-3.8(6)	2.8(6)
C1	42.9(12)	18.7(9)	17.3(8)	3.2(7)	0.3(8)	-2.6(8)
C2	13.3(7)	19.1(9)	15.9(8)	0.6(7)	2.6(6)	-1.9(6)
C3	13.5(8)	20.0(9)	15.0(8)	0.5(7)	2.4(6)	-2.2(6)
C4	15.3(8)	19.2(9)	13.7(7)	-0.2(7)	-0.9(6)	1.3(6)
C5	14.0(8)	20.5(9)	16.7(8)	2.8(7)	2.4(6)	-1.5(7)
C6	14.6(8)	19.8(9)	15.8(8)	-0.8(7)	2.5(6)	-2.2(7)
C7	13.5(7)	21.8(9)	13.7(7)	-0.9(7)	0.1(6)	-1.3(7)
C8	13.3(8)	18.1(8)	13.9(7)	0.5(7)	1.3(6)	-0.8(6)
C9	13.8(8)	17.3(8)	15.2(8)	-0.1(7)	-0.2(6)	-0.1(6)
C10	20.0(8)	17.1(8)	20.0(8)	0.0(7)	-0.2(7)	-2.4(7)
C11	24.8(9)	17.8(9)	21.1(9)	1.6(7)	0.5(7)	1.4(7)
C12	20.1(8)	19.7(9)	15.9(8)	2.5(7)	-0.8(6)	0.6(7)
C13	16.6(8)	21.7(9)	15.4(8)	0.0(7)	2.8(6)	1.7(7)
C14	18.8(8)	22.4(9)	14.7(8)	1.8(7)	4.3(6)	2.6(7)
C15	18.8(8)	21.2(9)	18.2(8)	2.1(7)	3.2(7)	1.5(7)
C16	15.4(8)	21.1(9)	20.5(8)	-0.9(7)	4.6(6)	0.8(7)
C17	35.5(11)	25.4(10)	22.4(10)	-6.1(8)	-5.3(8)	0.7(8)
O7	25.8(6)	20.8(7)	18.1(6)	-3.9(5)	-0.9(5)	-3.8(5)
O8	27.5(7)	25.7(7)	14.8(6)	0.6(5)	-2.3(5)	-0.8(6)
O9	16.4(6)	19.7(6)	18.9(6)	2.2(5)	1.5(5)	-3.9(5)
O10	13.9(6)	25.0(7)	28.8(7)	-5.2(6)	-0.2(5)	-2.2(5)
O11	29.2(7)	17.1(6)	20.4(6)	2.2(5)	-2.8(5)	3.5(5)
O12	37.7(8)	21.3(7)	21.5(7)	1.2(6)	-7.8(6)	-0.9(6)
C18	29.2(10)	26.3(10)	22.0(9)	-7.3(8)	-0.5(8)	-4.9(8)
C19	14.1(8)	21.1(9)	15.8(8)	-0.5(7)	3.0(6)	-2.9(6)
C20	13.9(7)	18.8(9)	15.8(8)	0.3(7)	4.1(6)	-1.3(7)
C21	16.6(8)	18.8(9)	12.7(7)	1.6(7)	-0.9(6)	-1.6(7)
C22	15.2(8)	16.9(8)	13.2(7)	1.1(6)	-1.6(6)	0.2(6)
C23	12.7(7)	18.0(8)	11.6(7)	0.5(7)	-0.5(6)	0.3(6)
C24	13.2(7)	17.2(8)	15.6(8)	0.2(7)	-0.3(6)	1.3(6)
C25	13.9(8)	18.6(9)	17.2(8)	-3.5(7)	2.7(6)	1.0(7)
C26	13.4(8)	16.9(8)	15.8(8)	-0.6(7)	2.1(6)	-0.8(6)
C27	23.0(9)	17.2(9)	18.4(8)	0.5(7)	-1.6(7)	2.9(7)
C28	21.5(9)	18.1(9)	18.6(8)	-2.2(7)	0.1(7)	2.1(7)
C29	17.8(8)	18.8(9)	14.1(8)	-1.5(7)	-1.8(6)	-2.0(7)
C30	14.9(7)	19.2(8)	13.2(7)	1.1(7)	0.2(6)	0.1(7)
C31	14.8(8)	20.8(9)	14.2(8)	-1.1(7)	2.4(6)	-0.9(6)
C32	18.3(8)	21.0(9)	14.9(8)	-1.0(7)	1.5(6)	1.6(7)

C33	16.1(8)	19.8(9)	17.8(8)	0.7(7)	2.1(7)	2.3(7)
C34	31.9(11)	21.4(10)	22.9(9)	5.0(8)	−2.4(8)	2.9(8)

Table S6 Bond Lengths for cu_0682_Cole_AM_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.447(2)	O7	C18	1.448(2)
O1	C2	1.340(2)	O7	C19	1.345(2)
O2	C2	1.208(2)	O8	C19	1.206(2)
O3	C4	1.472(2)	O9	C21	1.475(2)
O3	C5	1.352(2)	O9	C25	1.353(2)
O4	C5	1.203(2)	O10	C25	1.201(2)
O5	C16	1.205(2)	O11	C33	1.346(2)
O6	C16	1.342(2)	O11	C34	1.450(2)
O6	C17	1.446(2)	O12	C33	1.203(2)
C2	C3	1.478(2)	C19	C20	1.472(2)
C3	C4	1.504(3)	C20	C21	1.508(3)
C3	C6	1.333(2)	C20	C26	1.333(2)
C4	C9	1.537(2)	C21	C22	1.534(2)
C5	C7	1.517(3)	C22	C23	1.571(2)
C6	C7	1.509(3)	C22	C27	1.544(3)
C7	C8	1.576(2)	C23	C24	1.578(2)
C8	C9	1.567(2)	C23	C29	1.544(2)
C8	C12	1.545(3)	C23	C30	1.543(2)
C8	C13	1.542(2)	C24	C25	1.517(3)
C9	C10	1.545(2)	C24	C26	1.508(2)
C10	C11	1.536(3)	C27	C28	1.534(2)
C11	C12	1.538(3)	C28	C29	1.533(3)
C13	C14	1.500(2)	C30	C31	1.498(2)
C14	C15	1.323(3)	C31	C32	1.321(3)
C15	C16	1.484(3)	C32	C33	1.485(2)

Table S7 Bond Angles for cu_0682_Cole_AM_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	115.12(14)	C19	O7	C18	115.42(15)
C5	O3	C4	112.93(13)	C25	O9	C21	113.15(13)
C16	O6	C17	115.01(15)	C33	O11	C34	114.68(15)
O1	C2	C3	111.99(15)	O7	C19	C20	112.02(15)
O2	C2	O1	123.92(17)	O8	C19	O7	123.63(17)
O2	C2	C3	124.09(17)	O8	C19	C20	124.35(17)
C2	C3	C4	120.98(15)	C19	C20	C21	119.88(15)
C6	C3	C2	125.96(17)	C26	C20	C19	127.37(17)
C6	C3	C4	113.05(16)	C26	C20	C21	112.74(15)
O3	C4	C3	107.81(14)	O9	C21	C20	107.97(14)

O3	C4	C9	107.19(14)	O9	C21	C22	108.12(13)
C3	C4	C9	109.54(14)	C20	C21	C22	108.63(14)
O3	C5	C7	113.04(15)	C21	C22	C23	107.73(14)
O4	C5	O3	120.36(17)	C21	C22	C27	114.24(15)
O4	C5	C7	126.59(17)	C27	C22	C23	106.26(14)
C3	C6	C7	113.29(17)	C22	C23	C24	107.83(13)
C5	C7	C8	107.09(14)	C29	C23	C22	104.54(14)
C6	C7	C5	105.91(14)	C29	C23	C24	113.42(13)
C6	C7	C8	107.67(13)	C30	C23	C22	110.51(14)
C9	C8	C7	107.54(13)	C30	C23	C24	108.79(14)
C12	C8	C7	111.19(14)	C30	C23	C29	111.63(14)
C12	C8	C9	105.38(14)	C25	C24	C23	105.55(14)
C13	C8	C7	109.39(14)	C26	C24	C23	108.26(13)
C13	C8	C9	111.82(14)	C26	C24	C25	106.58(14)
C13	C8	C12	111.42(14)	O9	C25	C24	112.84(14)
C4	C9	C8	108.03(14)	O10	C25	O9	120.77(17)
C4	C9	C10	112.95(15)	O10	C25	C24	126.32(17)
C10	C9	C8	106.34(14)	C20	C26	C24	113.69(16)
C11	C10	C9	106.07(15)	C28	C27	C22	104.19(14)
C10	C11	C12	103.33(15)	C29	C28	C27	102.57(14)
C11	C12	C8	106.54(14)	C28	C29	C23	104.38(14)
C14	C13	C8	112.27(14)	C31	C30	C23	113.07(14)
C15	C14	C13	125.20(17)	C32	C31	C30	127.11(17)
C14	C15	C16	121.10(18)	C31	C32	C33	118.86(17)
O5	C16	O6	123.75(17)	O11	C33	C32	111.32(16)
O5	C16	C15	125.81(18)	O12	C33	O11	123.07(18)
O6	C16	C15	110.44(16)	O12	C33	C32	125.60(18)

Crystal Structure of *Endo*-32

Table S8 Crystal data and structure refinement for 0692_cole.

Identification code	0692_cole
Empirical formula	$C_{21}H_{20}O_6$
Formula weight	368.37
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6977(4)
b/Å	9.9164(4)
c/Å	20.6241(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1778.83(13)
Z	4
ρ_{calc}g/cm^3	1.375
μ/mm^{-1}	0.101

F(000)	776.0
Crystal size/mm^3	0.28 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.558 to 57.466
Index ranges	-10 ≤ h ≤ 11, -13 ≤ k ≤ 12, -27 ≤ l ≤ 27
Reflections collected	6802
Independent reflections	4513 [R_{int} = 0.0480, R_{sigma} = 0.0908]
Data/restraints/parameters	4513/0/254
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1017
Final R indexes [all data]	R_1 = 0.0795, wR_2 = 0.1140
Largest diff. peak/hole / e Å^{-3}	0.30/-0.25

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

$Goodness\text{-}of\text{-}fit = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S2

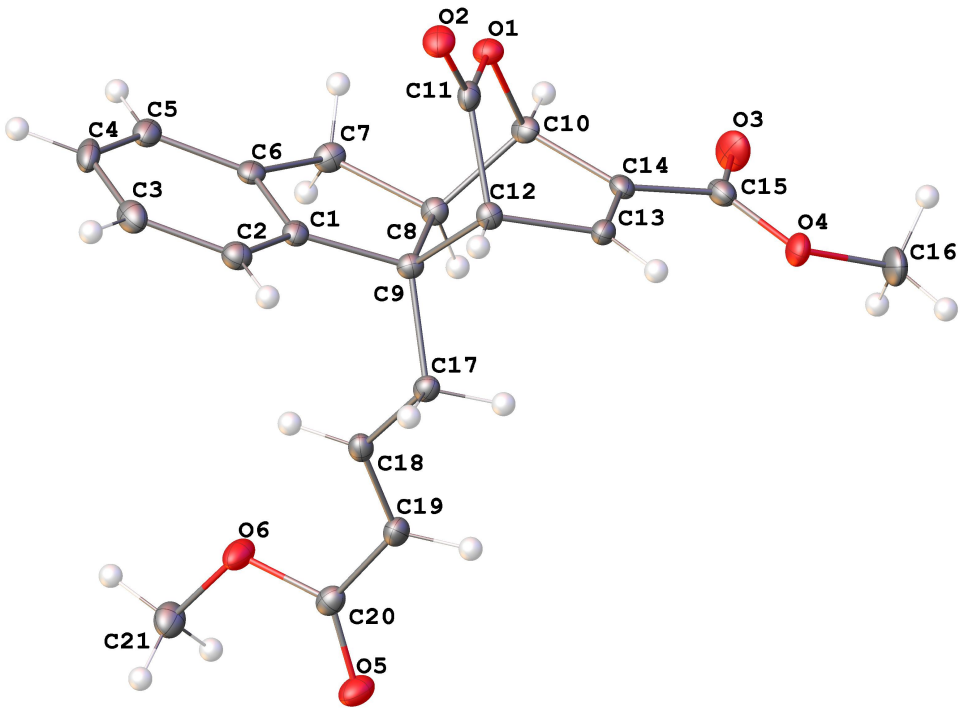


Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 0692_cole. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)

O1	2542(2)	2276.2(19)	6642.9(10)	17.5(5)
O2	4050(3)	1586(2)	7441.8(11)	22.0(5)
O3	-282(3)	5312(2)	6169.1(13)	30.9(6)
O4	739(2)	6603(2)	6952.0(11)	21.6(5)
O5	7568(3)	8069(2)	4417.8(11)	26.3(5)
O6	7612(3)	5838(2)	4241.8(11)	25.2(5)
C1	6159(3)	2657(3)	6149.7(14)	15.2(6)
C2	7516(4)	2333(3)	6466.8(15)	18.9(6)
C3	8299(4)	1163(3)	6289.8(16)	22.3(7)
C4	7712(4)	334(3)	5805.9(15)	22.2(7)
C5	6358(4)	656(3)	5492.3(16)	19.7(7)
C6	5583(3)	1828(3)	5668.0(14)	15.7(6)
C7	4097(4)	2370(3)	5395.9(16)	18.8(7)
C8	3729(3)	3629(3)	5807.0(15)	15.9(6)
C9	5125(3)	3858(3)	6275.6(15)	14.2(6)
C10	2283(4)	3445(3)	6219.3(15)	15.8(6)
C11	3715(4)	2458(3)	7063.3(14)	16.6(6)
C12	4481(3)	3814(3)	6988.6(14)	14.7(6)
C13	3232(3)	4863(3)	7054.1(15)	15.5(6)
C14	2072(3)	4666(3)	6646.9(15)	15.2(6)
C15	716(4)	5539(3)	6555.9(16)	19.1(7)
C16	-488(4)	7561(4)	6849(2)	31.3(8)
C17	5944(3)	5216(3)	6177.1(14)	15.3(6)
C18	6547(3)	5442(3)	5509.1(15)	16.3(6)
C19	6515(4)	6624(3)	5212.3(15)	19.0(7)
C20	7274(4)	6933(3)	4595.1(15)	18.2(6)
C21	8400(4)	6083(3)	3640.5(16)	25.0(8)

Table S10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 0692_cole. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	18.4(10)	15.8(10)	18.4(11)	3.3(8)	-0.5(9)	-1.2(9)
O2	26.6(12)	19.8(11)	19.7(12)	6.1(9)	2.4(9)	2.7(10)
O3	15.9(11)	31.8(13)	45.1(16)	-3.9(12)	-9.3(11)	5.5(11)
O4	19.8(11)	17.6(11)	27.4(13)	0.7(10)	2.7(9)	6.8(10)
O5	38.0(14)	16.4(10)	24.6(13)	1.9(9)	4.9(11)	-1.3(11)
O6	39.8(14)	15.3(10)	20.4(12)	0.7(9)	10.0(11)	0.4(11)
C1	17.3(14)	15.0(14)	13.3(15)	2.2(12)	2.7(12)	0.2(12)
C2	19.3(15)	19.5(14)	17.8(15)	1.1(12)	1.4(12)	-1.5(14)
C3	18.9(15)	23.2(16)	24.6(18)	6.6(14)	1.3(13)	4.5(14)
C4	27.7(16)	16.7(15)	22.3(17)	4.1(13)	9.9(14)	8.7(14)
C5	24.1(16)	16.8(15)	18.0(16)	2.1(13)	5.8(13)	-0.1(13)
C6	17.7(14)	14.5(14)	14.8(16)	3.6(12)	3.1(12)	-1.7(12)
C7	22.9(16)	18.5(15)	14.8(17)	0.0(13)	-2.6(12)	-0.8(14)
C8	15.4(13)	16.7(15)	15.6(15)	0.9(12)	-1.5(12)	0.9(12)

C9	15.4(14)	14.2(13)	12.9(15)	0.5(12)	-0.9(11)	-0.6(12)
C10	14.8(13)	14.5(13)	18.1(15)	4.1(12)	-2.2(12)	1.7(12)
C11	18.2(14)	17.1(14)	14.6(15)	-1.4(13)	3.6(12)	3.5(12)
C12	14.8(13)	16.5(15)	12.6(15)	-0.2(12)	-0.8(12)	0.3(12)
C13	16.6(13)	13.1(14)	16.8(15)	-0.6(12)	3.1(12)	0.2(12)
C14	13.8(14)	15.4(14)	16.3(15)	2.8(12)	4.4(11)	-0.4(12)
C15	14.6(14)	19.3(15)	23.2(17)	4.8(13)	2.9(13)	0.4(13)
C16	19.5(16)	26.6(18)	48(2)	-0.7(17)	6.8(15)	10.1(15)
C17	14.6(14)	14.3(13)	17.1(16)	-0.6(12)	-1.4(12)	0.1(12)
C18	14.1(14)	17.2(15)	17.6(15)	-3.2(12)	0.6(12)	0.2(12)
C19	19.8(15)	16.1(15)	21.0(16)	-3.6(13)	2.8(13)	0.5(13)
C20	18.5(14)	16.3(14)	19.9(17)	-0.7(12)	-3.3(13)	1.1(13)
C21	32.4(19)	24.5(16)	18.1(17)	2.0(14)	5.9(14)	3.8(16)

Table S11 Bond Lengths for 0692_cole.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.469(3)	C5	C6	1.392(4)
O1	C11	1.352(4)	C6	C7	1.508(4)
O2	C11	1.201(4)	C7	C8	1.543(4)
O3	C15	1.201(4)	C8	C9	1.568(4)
O4	C15	1.335(4)	C8	C10	1.529(4)
O4	C16	1.445(4)	C9	C12	1.574(4)
O5	C20	1.211(4)	C9	C17	1.537(4)
O6	C20	1.341(4)	C10	C14	1.509(4)
O6	C21	1.438(4)	C11	C12	1.509(4)
C1	C2	1.387(4)	C12	C13	1.511(4)
C1	C6	1.384(4)	C13	C14	1.327(4)
C1	C9	1.515(4)	C14	C15	1.475(4)
C2	C3	1.394(4)	C17	C18	1.491(4)
C3	C4	1.390(5)	C18	C19	1.322(4)
C4	C5	1.381(5)	C19	C20	1.467(5)

Table S12 Bond Angles for 0692_cole.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O1	C10	113.1(2)	O1	C10	C8	107.4(2)
C15	O4	C16	114.8(3)	O1	C10	C14	107.7(2)
C20	O6	C21	115.9(2)	C14	C10	C8	109.2(2)
C2	C1	C9	127.4(3)	O1	C11	C12	112.7(2)
C6	C1	C2	120.6(3)	O2	C11	O1	120.3(3)
C6	C1	C9	112.0(3)	O2	C11	C12	127.0(3)
C1	C2	C3	119.0(3)	C11	C12	C9	106.1(2)
C4	C3	C2	120.0(3)	C11	C12	C13	106.7(2)
C5	C4	C3	120.8(3)	C13	C12	C9	108.7(2)

C4	C5	C6	119.0(3)	C14	C13	C12	112.9(3)
C1	C6	C5	120.5(3)	C13	C14	C10	113.3(3)
C1	C6	C7	111.4(3)	C13	C14	C15	127.0(3)
C5	C6	C7	128.1(3)	C15	C14	C10	119.6(3)
C6	C7	C8	105.2(3)	O3	C15	O4	124.4(3)
C7	C8	C9	107.2(2)	O3	C15	C14	123.6(3)
C10	C8	C7	112.3(2)	O4	C15	C14	112.0(3)
C10	C8	C9	108.1(2)	C18	C17	C9	114.6(2)
C1	C9	C8	103.9(2)	C19	C18	C17	123.6(3)
C1	C9	C12	110.5(2)	C18	C19	C20	125.3(3)
C1	C9	C17	113.0(2)	O5	C20	O6	122.9(3)
C8	C9	C12	107.2(2)	O5	C20	C19	123.5(3)
C17	C9	C8	113.8(2)	O6	C20	C19	113.6(3)
C17	C9	C12	108.2(2)				

Crystal Structure of *Endo*-36

Table S13 Crystal data and structure refinement for 0685_cole.

Identification code	0685_cole
Empirical formula	$C_{20}H_{20}O_6$
Formula weight	356.36
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1979(9)
b/Å	12.5205(10)
c/Å	24.904(2)
α/°	90
β/°	93.401(2)
γ/°	90
Volume/Å^3	3485.5(5)
Z	8
ρ_{calc}g/cm^3	1.358
μ/mm^{-1}	0.100
F(000)	1504.0
Crystal size/mm^3	0.32 × 0.16 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.618 to 50.92
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30
Reflections collected	41322
Independent reflections	6449 [R_{int} = 0.0939, R_{sigma} = 0.0747]
Data/restraints/parameters	6449/0/473
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0846, wR_2 = 0.1990
Final R indexes [all data]	R_1 = 0.1373, wR_2 = 0.2260
Largest diff. peak/hole / e Å^{-3}	0.85/-0.31

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma |F_o|$

$wR2 = [\Sigma \, [w \, (F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w \, (F_o^2)^{\,2}]]^{1/2}$

Goodness-of-fit = $[\Sigma \, [w \, (F_o^2 - F_c^2)^{\,2}] \, / \, (n-p)^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S3

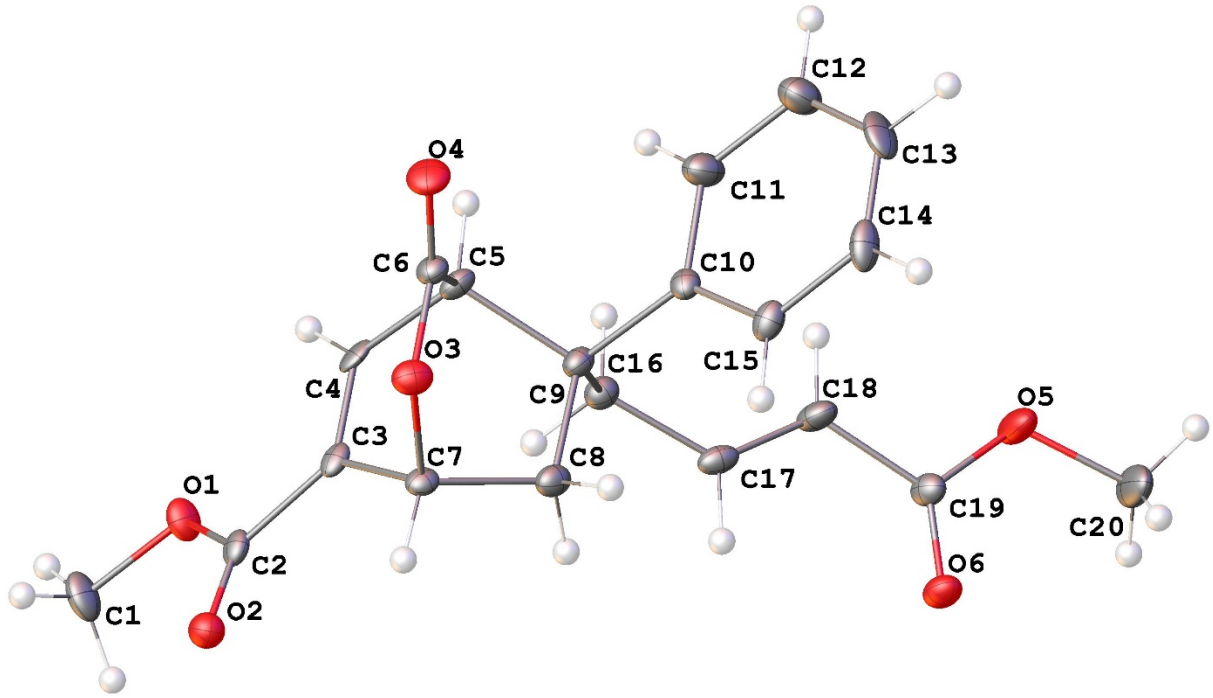


Table S14 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 0685_cole. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7906(2)	1870(2)	8304.9(11)	22.2(7)
O2	9647(2)	2234(2)	8768.7(11)	22.4(7)
O3	10691(2)	4097(2)	7611.0(11)	22.0(7)
O4	9894(3)	5210(2)	7001.7(12)	26.8(7)
O5	11417(3)	-575(3)	5209.1(12)	34.0(8)
O6	12305(2)	-777(2)	6028.1(11)	24.1(7)
C1	7442(4)	1468(4)	8792.2(17)	28.7(11)
C2	9026(3)	2230(3)	8357.6(16)	17.0(9)
C3	9395(3)	2661(3)	7836.2(16)	15.7(9)
C4	8683(3)	2861(3)	7407.7(16)	15.6(9)
C5	9298(3)	3339(3)	6954.0(16)	16.8(9)
C6	9963(3)	4314(3)	7172.6(16)	16.7(9)
C7	10677(3)	2963(3)	7760.0(16)	16.0(9)
C8	11135(3)	2354(3)	7280.7(16)	19.6(9)
C9	10296(3)	2534(3)	6775.6(16)	17.0(9)
C10	10871(3)	3002(3)	6281.2(16)	16.2(9)
C11	10117(4)	3279(4)	5833.7(17)	27.7(11)

C12	10559(4)	3662(4)	5364.4(18)	31.4(11)
C13	11778(4)	3777(4)	5336.2(19)	31.2(11)
C14	12537(4)	3525(3)	5767.8(18)	26.3(10)
C15	12082(4)	3114(3)	6233.9(17)	20.1(9)
C16	9679(3)	1455(3)	6605.3(17)	18.9(9)
C17	10553(3)	678(3)	6401.3(17)	19.2(9)
C18	10596(4)	361(3)	5896.7(17)	23.9(10)
C19	11524(4)	-389(3)	5739.0(16)	19.8(9)
C20	12310(5)	-1268(4)	4993.0(19)	43.1(14)
O7	5339(2)	5233(2)	6193.0(10)	17.9(6)
O8	7083(2)	5502(2)	6672.6(11)	18.5(6)
O9	4192(2)	3297(2)	7314.5(11)	21.1(7)
O10	4916(3)	2157(2)	7925.6(12)	26.7(7)
O11	2954(2)	8243(2)	9037.7(11)	21.8(7)
O12	4377(3)	8322(2)	9717.8(11)	26.2(7)
C21	7579(4)	5958(4)	6200.2(17)	25.3(10)
C22	5954(3)	5174(3)	6606.2(15)	13.6(8)
C23	5555(3)	4703(3)	7107.6(15)	12.4(8)
C24	6235(3)	4478(3)	7547.4(15)	14.7(8)
C25	5580(3)	3999(3)	7992.6(16)	17.2(9)
C26	4891(3)	3052(3)	7760.4(15)	16.9(9)
C27	4262(3)	4439(3)	7167.0(15)	13.5(8)
C28	3799(3)	5052(3)	7641.0(15)	17.9(9)
C29	4598(3)	4844(3)	8153.6(15)	15.8(9)
C30	3953(3)	4393(3)	8632.1(15)	14.0(8)
C31	2738(4)	4376(3)	8663.4(17)	20.8(9)
C32	2204(4)	3963(4)	9111.3(18)	27.4(11)
C33	2890(4)	3590(4)	9539.9(18)	29.3(11)
C34	4110(4)	3608(5)	9519(2)	45.0(15)
C35	4635(4)	4006(4)	9075.5(18)	37.3(13)
C36	5285(3)	5871(3)	8338.3(16)	16.5(9)
C37	4489(3)	6685(3)	8563.9(16)	17.3(9)
C38	4696(4)	7137(3)	9038.2(16)	21.0(9)
C39	3901(4)	7940(3)	9245.6(16)	18.7(9)
C40	3717(4)	9147(4)	9970.6(18)	28.6(11)

Table S15 Anisotropic Displacement Parameters ($Å^2×10^3$) for 0685_cole. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	22.1(15)	23.3(16)	21.8(16)	-1.1(13)	6.5(13)	-8.9(13)
O2	23.3(15)	22.4(16)	21.6(16)	0.5(13)	1.5(13)	1.2(13)
O3	20.2(15)	18.5(15)	27.1(16)	2.3(13)	-1.3(13)	-3.3(13)
O4	35.0(18)	12.2(16)	33.4(18)	4.2(13)	3.9(14)	0.7(13)
O5	39.3(19)	38(2)	23.6(17)	-6.3(15)	-4.6(15)	23.0(16)
O6	22.8(15)	26.7(17)	22.0(16)	-1.3(13)	-4.6(13)	6.9(14)

C1	34(3)	30(3)	24(2)	0(2)	14(2)	−12(2)
C2	19(2)	11(2)	22(2)	−3.7(17)	7.8(19)	1.1(17)
C3	16(2)	6.3(19)	26(2)	−2.3(17)	6.4(18)	0.1(16)
C4	12.3(19)	6.4(19)	28(2)	−4.0(17)	1.7(18)	3.9(16)
C5	11.9(19)	13(2)	26(2)	−0.6(17)	−1.1(17)	1.4(16)
C6	18(2)	12(2)	19(2)	0.6(17)	1.4(18)	2.5(17)
C7	17(2)	11(2)	21(2)	3.1(16)	1.4(17)	−0.6(16)
C8	15(2)	20(2)	24(2)	4.6(18)	2.3(18)	0.3(18)
C9	15(2)	14(2)	22(2)	1.9(17)	3.2(17)	1.8(17)
C10	20(2)	10(2)	19(2)	0.3(16)	4.3(17)	0.5(17)
C11	25(2)	31(3)	27(2)	9(2)	1(2)	2(2)
C12	32(3)	38(3)	25(2)	8(2)	1(2)	2(2)
C13	46(3)	24(2)	26(3)	5(2)	21(2)	−7(2)
C14	25(2)	22(2)	33(3)	−8(2)	16(2)	−9(2)
C15	17(2)	16(2)	27(2)	−6.3(18)	4.0(18)	−1.6(17)
C16	17(2)	17(2)	22(2)	0.5(18)	1.0(18)	0.0(17)
C17	13.4(19)	15(2)	29(2)	4.9(18)	−2.9(18)	−1.0(17)
C18	23(2)	21(2)	26(2)	−1.0(19)	−5.7(19)	8.5(19)
C19	25(2)	16(2)	18(2)	−3.8(17)	−2.1(19)	3.2(18)
C20	60(3)	46(3)	24(3)	−8(2)	4(2)	31(3)
O7	20.5(15)	20.5(15)	12.4(15)	1.4(12)	−0.9(12)	2.7(12)
O8	17.2(14)	19.2(15)	19.1(15)	2.0(12)	0.1(12)	−5.1(12)
O9	24.9(16)	12.7(14)	25.1(16)	−0.3(12)	−4.9(13)	−4.2(12)
O10	44.6(19)	8.8(15)	26.9(17)	0.9(13)	3.6(14)	−3.8(14)
O11	16.6(15)	21.5(16)	27.0(16)	1.4(13)	−1.0(13)	−1.4(13)
O12	28.5(16)	31.5(18)	18.3(16)	−0.6(13)	0.0(13)	9.2(14)
C21	24(2)	29(3)	24(2)	8(2)	3.8(19)	−6(2)
C22	16(2)	6.2(19)	18(2)	−4.0(16)	1.0(18)	2.1(16)
C23	14.2(19)	6.9(19)	16(2)	−4.3(15)	1.5(17)	1.8(15)
C24	16.1(19)	7.7(19)	20(2)	−1.8(16)	−3.0(17)	1.7(16)
C25	15(2)	16(2)	21(2)	2.5(17)	−3.0(17)	0.7(17)
C26	22(2)	14(2)	15(2)	−1.8(17)	0.3(17)	−0.1(17)
C27	13.6(19)	7.7(19)	19(2)	3.5(16)	−4.9(16)	−3.9(16)
C28	15(2)	17(2)	22(2)	3.6(17)	0.9(17)	0.1(17)
C29	18(2)	11(2)	18(2)	0.6(16)	1.9(17)	2.2(17)
C30	17(2)	9.4(19)	15(2)	−0.5(16)	0.5(16)	−2.0(16)
C31	19(2)	21(2)	22(2)	−3.3(18)	0.0(18)	1.2(18)
C32	20(2)	30(3)	34(3)	−6(2)	8(2)	−4(2)
C33	37(3)	28(3)	25(3)	6(2)	15(2)	1(2)
C34	32(3)	72(4)	31(3)	31(3)	3(2)	15(3)
C35	21(2)	63(4)	28(3)	23(2)	3(2)	8(2)
C36	13.9(19)	16(2)	19(2)	0.0(17)	−2.1(17)	0.7(17)
C37	16(2)	15(2)	20(2)	3.3(17)	−4.1(17)	−2.1(17)
C38	24(2)	18(2)	21(2)	−0.3(18)	−2.7(18)	4.8(18)
C39	28(2)	12(2)	17(2)	−0.6(17)	4.6(19)	1.9(18)
C40	35(3)	28(3)	23(2)	−3(2)	9(2)	2(2)

Table S16 Bond Lengths for 0685_cole.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.439(5)	O7	C22	1.206(4)
O1	C2	1.332(5)	O8	C21	1.448(5)
O2	C2	1.203(5)	O8	C22	1.329(4)
O3	C6	1.351(5)	O9	C26	1.355(5)
O3	C7	1.467(5)	O9	C27	1.479(4)
O4	C6	1.201(5)	O10	C26	1.193(5)
O5	C19	1.338(5)	O11	C39	1.213(5)
O5	C20	1.451(5)	O12	C39	1.350(5)
O6	C19	1.202(5)	O12	C40	1.437(5)
C2	C3	1.487(6)	C22	C23	1.474(5)
C3	C4	1.317(5)	C23	C24	1.327(5)
C3	C7	1.508(5)	C23	C27	1.501(5)
C4	C5	1.484(6)	C24	C25	1.491(6)
C5	C6	1.514(5)	C25	C26	1.511(5)
C5	C9	1.589(5)	C25	C29	1.594(5)
C7	C8	1.531(5)	C27	C28	1.524(5)
C8	C9	1.541(5)	C28	C29	1.537(5)
C9	C10	1.539(5)	C29	C30	1.537(5)
C9	C16	1.564(5)	C29	C36	1.554(5)
C10	C11	1.402(6)	C30	C31	1.368(5)
C10	C15	1.375(5)	C30	C35	1.392(6)
C11	C12	1.381(6)	C31	C32	1.396(6)
C12	C13	1.379(6)	C32	C33	1.360(6)
C13	C14	1.367(6)	C33	C34	1.371(7)
C14	C15	1.393(6)	C34	C35	1.375(6)
C16	C17	1.490(6)	C36	C37	1.486(5)
C17	C18	1.321(6)	C37	C38	1.318(6)
C18	C19	1.471(6)	C38	C39	1.458(6)

Table S17 Bond Angles for 0685_cole.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	114.9(3)	C22	O8	C21	115.4(3)
C6	O3	C7	112.6(3)	C26	O9	C27	112.7(3)
C19	O5	C20	116.5(3)	C39	O12	C40	116.7(3)
O1	C2	C3	110.2(3)	O7	C22	O8	125.3(4)
O2	C2	O1	125.4(4)	O7	C22	C23	124.1(3)
O2	C2	C3	124.4(4)	O8	C22	C23	110.6(3)
C2	C3	C7	121.1(3)	C22	C23	C27	121.0(3)
C4	C3	C2	126.2(4)	C24	C23	C22	126.6(4)
C4	C3	C7	112.7(4)	C24	C23	C27	112.4(3)
C3	C4	C5	114.1(3)	C23	C24	C25	114.5(3)

C4	C5	C6	107.0(3)	C24	C25	C26	107.1(3)
C4	C5	C9	108.8(3)	C24	C25	C29	107.3(3)
C6	C5	C9	105.9(3)	C26	C25	C29	105.8(3)
O3	C6	C5	112.9(3)	O9	C26	C25	113.2(3)
O4	C6	O3	119.8(4)	O10	C26	O9	119.7(4)
O4	C6	C5	127.3(4)	O10	C26	C25	127.2(4)
O3	C7	C3	107.4(3)	O9	C27	C23	107.6(3)
O3	C7	C8	106.0(3)	O9	C27	C28	105.6(3)
C3	C7	C8	109.8(3)	C23	C27	C28	109.8(3)
C7	C8	C9	110.3(3)	C27	C28	C29	110.5(3)
C8	C9	C5	105.6(3)	C28	C29	C25	106.2(3)
C8	C9	C16	109.5(3)	C28	C29	C30	115.4(3)
C10	C9	C5	108.5(3)	C28	C29	C36	111.0(3)
C10	C9	C8	116.4(3)	C30	C29	C25	108.3(3)
C10	C9	C16	108.1(3)	C30	C29	C36	108.8(3)
C16	C9	C5	108.5(3)	C36	C29	C25	106.7(3)
C11	C10	C9	118.0(4)	C31	C30	C29	124.4(4)
C15	C10	C9	124.7(4)	C31	C30	C35	116.8(4)
C15	C10	C11	117.2(4)	C35	C30	C29	118.8(3)
C12	C11	C10	122.0(4)	C30	C31	C32	121.7(4)
C13	C12	C11	119.0(4)	C33	C32	C31	120.4(4)
C14	C13	C12	120.5(4)	C32	C33	C34	118.8(4)
C13	C14	C15	120.0(4)	C33	C34	C35	120.8(4)
C10	C15	C14	121.3(4)	C34	C35	C30	121.5(4)
C17	C16	C9	111.6(3)	C37	C36	C29	112.5(3)
C18	C17	C16	125.6(4)	C38	C37	C36	123.8(4)
C17	C18	C19	120.8(4)	C37	C38	C39	122.3(4)
O5	C19	C18	110.6(3)	O11	C39	O12	123.4(4)
O6	C19	O5	122.6(4)	O11	C39	C38	127.0(4)
O6	C19	C18	126.8(4)	O12	C39	C38	109.6(3)

Crystal Structure of *Endo*-40

Table S18 Crystal data and structure refinement for 0683_cole.

Identification code	0683_cole
Empirical formula	$C_{18}H_{18}O_7$
Formula weight	346.32
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6526(8)
b/Å	9.7720(5)
c/Å	24.8831(13)
α/°	90
β/°	101.015(2)
γ/°	90
Volume/Å^3	3258.6(3)

Z	8
ρ_{calc}g/cm^3	1.412
μ/mm^{-1}	0.109
F(000)	1456.0
Crystal size/mm^3	0.384 × 0.184 × 0.171
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.49 to 48.29
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -28 ≤ l ≤ 28
Reflections collected	45288
Independent reflections	5139 [R_{int} = 0.0269, R_{sigma} = 0.0146]
Data/restraints/parameters	5139/42/505
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0847
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.0886
Largest diff. peak/hole / e Å^{-3}	0.20/-0.24

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

Goodness-of-fit = $[\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S4

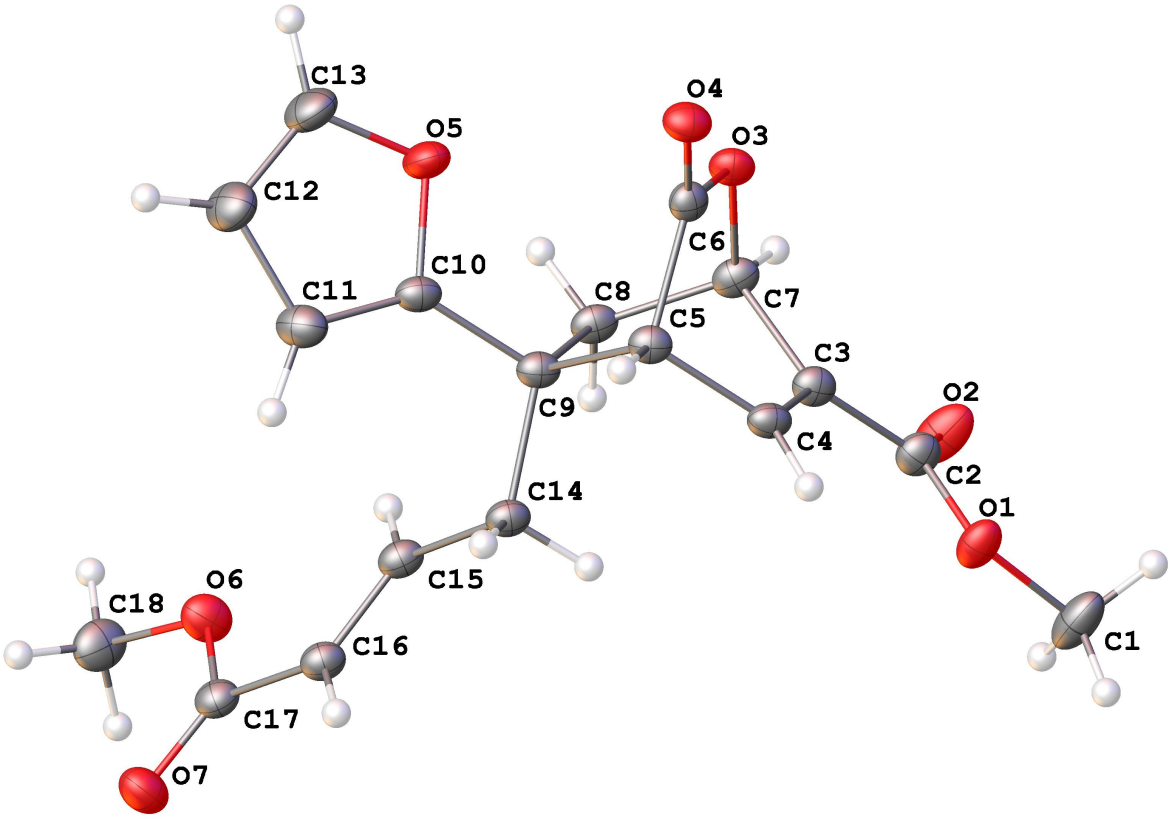


Table S19 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 0683_cole. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3295.0(9)	2872.6(11)	8659.7(5)	29.0(3)
O2	3213.1(11)	575.5(12)	8679.3(5)	41.6(3)
O3	5009.4(8)	552.1(11)	7520.7(4)	24.1(3)
O4	5880.5(8)	2000.4(12)	7109.2(5)	27.4(3)
O5	4351.6(9)	381.8(12)	6235.6(5)	30.8(3)
O6	-99.5(9)	80.6(12)	5787.1(5)	31.9(3)
O7	-914.0(9)	1980.8(13)	5456.6(5)	34.4(3)
C1	2879.1(17)	2926(2)	9149.6(8)	42.1(5)
C2	3413.9(13)	1617.9(17)	8466.1(7)	26.4(4)
C3	3788.4(12)	1676.0(16)	7949.1(7)	23.0(4)
C4	3858.9(11)	2794.2(16)	7655.9(7)	22.2(4)
C5	4132.0(11)	2509.0(16)	7109.2(6)	21.2(3)
C6	5093.2(12)	1702.6(16)	7229.9(6)	21.7(4)
C7	4019.4(12)	394.0(16)	7665.0(7)	24.0(4)
C8	3266.1(12)	237.3(16)	7129.3(7)	23.4(4)
C9	3293.6(12)	1550.9(16)	6775.3(7)	21.4(4)
C10	3553.2(12)	1241.5(16)	6227.9(7)	23.0(4)
C11	3204.3(13)	1658.5(18)	5713.1(7)	31.4(4)
C12	3805.6(14)	1022(2)	5374.1(8)	37.5(5)
C13	4487.6(15)	280(2)	5706.8(8)	37.2(5)
C14	2300.0(11)	2345.0(16)	6695.0(7)	22.8(4)
C15	1426.0(12)	1594.6(16)	6371.1(6)	23.2(4)
C16	642.0(12)	2195.3(17)	6066.3(7)	23.8(4)
C17	-203.8(12)	1445.3(17)	5744.1(7)	24.5(4)
C18	-876.9(14)	-718.0(19)	5456.5(8)	36.4(4)
O8	2465.2(9)	2086.6(12)	1143.5(5)	28.3(3)
O9	2308.8(9)	4382.8(12)	1116.1(5)	30.8(3)
O10	4791.6(8)	4752.1(11)	2273.8(5)	25.9(3)
O11	6120.2(8)	3573.8(13)	2678.1(5)	33.1(3)
O12	4919.4(10)	2870.7(12)	3886.7(5)	35.4(3)
C19	1837.4(13)	2037.5(19)	608.0(7)	32.4(4)
C20	2672.0(12)	3352.7(17)	1337.9(7)	24.7(4)
C21	3399.2(12)	3343.9(16)	1859.4(7)	22.9(4)
C22	3811.2(12)	2262.0(16)	2137.7(7)	22.1(4)
C23	4467.4(12)	2631.2(16)	2675.7(6)	21.5(4)
C24	5226.6(12)	3647.5(17)	2551.9(6)	24.2(4)
C25	3699.2(12)	4673.0(17)	2148.6(7)	24.4(4)
C26	3336.8(12)	4668.1(16)	2693.1(7)	24.6(4)
C27	3821.7(12)	3437.6(16)	3035.7(7)	22.7(4)
C28	4489.9(12)	3910.2(17)	3550.8(7)	25.6(4)
C29	4759.6(13)	5128.2(18)	3787.1(7)	29.6(4)
C30	5399.2(15)	4846(2)	4300.6(8)	39.2(5)
C31	5465.9(16)	3484(2)	4342.8(8)	43.4(5)

C32	3027.3(13)	2441.1(17)	3181.5(7)	28.8(4)
O13A	405(4)	4451(7)	3994(3)	42.2(12)
O14A	1871(4)	4069(6)	4543(2)	27.9(11)
C33A	2607(4)	2993(3)	3673(2)	24.5(9)
C34A	1690(3)	3463(3)	3616.1(13)	26.8(11)
C35A	1236(6)	4049(9)	4054(4)	26.8(19)
C36A	1480(6)	4689(12)	4991(4)	40.7(17)
O13B	807(8)	4457(13)	3949(4)	39(3)
O14B	1888(9)	3974(13)	4749(4)	31(2)
C33B	2241(5)	3164(5)	3411(3)	20.5(18)
C34B	2309(5)	3197(6)	3948(3)	28.5(19)
C35B	1570(9)	3944(16)	4204(6)	20(3)
C36B	1182(13)	4630(20)	5023(9)	40.7(17)

Table S20 Anisotropic Displacement Parameters ($Å^2×10^3$) for 0683_cole. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	44.9(7)	17.7(6)	26.6(6)	−1.6(5)	11.9(5)	0.4(5)
O2	70.3(10)	19.2(7)	43.5(8)	2.9(6)	31.4(7)	−4.2(6)
O3	25.7(6)	16.6(6)	30.0(6)	1.7(5)	5.6(5)	3.5(5)
O4	21.0(6)	25.6(6)	35.6(7)	−0.8(5)	5.7(5)	−0.9(5)
O5	31.8(7)	31.9(7)	30.3(6)	−0.8(5)	10.0(5)	10.4(5)
O6	31.3(7)	22.1(6)	40.7(7)	−1.5(5)	2.6(6)	−3.5(5)
O7	29.4(7)	31.7(7)	38.7(7)	−0.3(6)	−2.1(6)	3.2(6)
C1	71.8(15)	27.9(10)	32.1(10)	−2.3(8)	23.7(10)	5.0(10)
C2	31.8(10)	18.4(9)	29.3(9)	−1.5(8)	6.9(7)	−0.2(7)
C3	23.7(9)	16.6(8)	28.6(9)	−0.6(7)	4.6(7)	−1.6(6)
C4	19.3(8)	17.0(8)	30.3(9)	−1.9(7)	4.7(7)	0.5(6)
C5	21.5(8)	15.7(8)	27.2(8)	2.3(7)	6.4(7)	−1.4(6)
C6	24.4(9)	17.1(8)	23.2(8)	−2.2(7)	3.8(7)	−1.5(7)
C7	29.4(9)	15.6(8)	29.3(9)	2.5(7)	11.1(7)	0.4(7)
C8	25.4(9)	14.8(8)	31.6(9)	−0.6(7)	9.6(7)	−1.7(7)
C9	19.9(8)	16.8(8)	28.0(9)	0.1(7)	6.1(7)	−0.7(6)
C10	20.3(8)	18.3(8)	31.2(9)	−0.6(7)	7.3(7)	0.5(7)
C11	30.3(10)	31.9(10)	34.1(10)	7.5(8)	11.1(8)	4.6(8)
C12	41.5(11)	44.3(11)	30.4(10)	4.6(9)	15.9(9)	4.8(9)
C13	40.5(11)	40.6(11)	35.2(10)	−2.0(9)	19.0(9)	7.6(9)
C14	22.8(9)	17.8(8)	28.8(9)	−0.7(7)	7.5(7)	0.4(7)
C15	25.2(9)	18.2(8)	28.4(9)	−0.5(7)	10.7(7)	−0.8(7)
C16	24.9(9)	19.5(8)	28.6(9)	−0.1(7)	8.9(7)	0.1(7)
C17	24.4(9)	24.9(9)	26.3(9)	0.1(7)	10.2(7)	0.6(7)
C18	34.0(10)	30.2(10)	45.6(11)	−9.3(9)	9.5(9)	−10.3(8)
O8	31.2(7)	24.9(6)	26.1(6)	−2.6(5)	−1.1(5)	−3.1(5)
O9	32.6(7)	28.5(7)	29.9(6)	4.3(6)	2.4(5)	4.0(5)
O10	23.4(6)	22.8(6)	32.2(6)	−1.1(5)	7.2(5)	−4.7(5)

O11	18.5(7)	43.8(8)	37.3(7)	−7.0(6)	6.2(5)	0.2(5)
O12	45.6(8)	29.7(7)	28.3(7)	−2.0(5)	0.7(6)	5.7(6)
C19	31.6(10)	37.1(10)	26.2(9)	−3.8(8)	−0.2(8)	−5.4(8)
C20	24.1(9)	23.4(9)	27.5(9)	0.7(8)	7.3(7)	−1.1(7)
C21	22.2(9)	20.2(8)	27.0(9)	−1.0(7)	6.5(7)	−2.1(7)
C22	22.4(9)	18.0(8)	27.1(9)	−3.4(7)	7.7(7)	−1.0(7)
C23	21.1(8)	17.9(8)	25.4(8)	−1.8(7)	4.0(7)	3.1(6)
C24	23.2(10)	26.6(9)	23.5(8)	−8.3(7)	6.3(7)	0.6(7)
C25	21.1(9)	18.7(8)	32.5(9)	1.3(7)	2.8(7)	0.0(7)
C26	22.5(9)	16.0(8)	35.9(9)	−2.5(7)	7.2(7)	0.2(7)
C27	22.0(9)	17.8(8)	29.4(9)	−2.1(7)	7.8(7)	0.7(7)
C28	28.5(9)	23.8(9)	26.6(9)	0.7(7)	10.9(7)	2.2(7)
C29	35.8(10)	27.3(9)	28.7(9)	−6.3(8)	13.9(8)	−5.7(8)
C30	44.5(12)	43.7(12)	29.8(10)	−13.4(9)	7.9(9)	−6.9(9)
C31	51.0(13)	50.1(13)	25.0(10)	−6.1(9)	−2.9(9)	5.2(10)
C32	30.8(10)	18.8(8)	40.1(10)	−2.1(8)	15.2(8)	−2.9(7)
O13A	29(3)	45.9(19)	50(2)	−14.2(15)	4.0(18)	1(2)
O14A	34.0(17)	27.5(16)	21(3)	3(3)	3(3)	4.8(11)
C33A	26(2)	22.6(16)	23(2)	5.6(16)	0.5(17)	−6.1(15)
C34A	27(2)	27.1(16)	25.2(17)	0.0(13)	1.5(16)	−3.0(13)
C35A	34(6)	19(3)	26(5)	1(3)	2(3)	−2(4)
C36A	62(6)	29.7(15)	33.7(17)	−4.5(13)	17(3)	−4(4)
O13B	45(9)	40(5)	32(3)	−1(3)	9(5)	0(6)
O14B	48(3)	32(3)	14(4)	0(4)	6(4)	0(2)
C33B	17(3)	20(3)	22(4)	3(2)	0(3)	−4(2)
C34B	26(3)	33(3)	27(4)	6(3)	6(3)	−2(2)
C35B	23(7)	23(4)	14(8)	4(5)	3(5)	1(5)
C36B	62(6)	29.7(15)	33.7(17)	−4.5(13)	17(3)	−4(4)

Table S21 Bond Lengths for 0683_cole.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.441(2)	O10	C24	1.356(2)
O1	C2	1.338(2)	O10	C25	1.466(2)
O2	C2	1.204(2)	O11	C24	1.202(2)
O3	C6	1.354(2)	O12	C28	1.374(2)
O3	C7	1.471(2)	O12	C31	1.371(2)
O4	C6	1.2056(19)	C20	C21	1.476(2)
O5	C10	1.3735(19)	C21	C22	1.329(2)
O5	C13	1.367(2)	C21	C25	1.503(2)
O6	C17	1.343(2)	C22	C23	1.506(2)
O6	C18	1.442(2)	C23	C24	1.509(2)
O7	C17	1.209(2)	C23	C27	1.582(2)
C2	C3	1.474(2)	C25	C26	1.529(2)
C3	C4	1.328(2)	C26	C27	1.548(2)
C3	C7	1.501(2)	C27	C28	1.497(2)

C4	C5	1.504(2)	C27	C32	1.551(2)
C5	C6	1.511(2)	C28	C29	1.347(2)
C5	C9	1.585(2)	C29	C30	1.430(3)
C7	C8	1.528(2)	C30	C31	1.337(3)
C8	C9	1.561(2)	C32	C33A	1.543(5)
C9	C10	1.502(2)	C32	C33B	1.487(7)
C9	C14	1.542(2)	O13A	C35A	1.183(10)
C10	C11	1.342(2)	O14A	C35A	1.353(7)
C11	C12	1.427(3)	O14A	C36A	1.456(10)
C12	C13	1.335(3)	C33A	C34A	1.316(8)
C14	C15	1.498(2)	C34A	C35A	1.468(10)
C15	C16	1.325(2)	O13B	C35B	1.220(13)
C16	C17	1.470(2)	O14B	C35B	1.343(11)
O8	C19	1.441(2)	O14B	C36B	1.434(19)
O8	C20	1.339(2)	C33B	C34B	1.322(13)
O9	C20	1.208(2)	C34B	C35B	1.484(15)

Table S22 Bond Angles for 0683_cole.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	115.59(13)	O9	C20	O8	124.41(15)
C6	O3	C7	113.14(12)	O9	C20	C21	123.72(15)
C13	O5	C10	106.52(13)	C20	C21	C25	119.47(14)
C17	O6	C18	115.90(14)	C22	C21	C20	127.57(15)
O1	C2	C3	111.41(14)	C22	C21	C25	112.87(14)
O2	C2	O1	124.26(15)	C21	C22	C23	113.18(14)
O2	C2	C3	124.29(15)	C22	C23	C24	106.94(13)
C2	C3	C7	121.20(14)	C22	C23	C27	108.75(13)
C4	C3	C2	125.82(15)	C24	C23	C27	105.46(12)
C4	C3	C7	112.60(14)	O10	C24	C23	112.15(13)
C3	C4	C5	113.65(14)	O11	C24	O10	120.29(15)
C4	C5	C6	105.84(13)	O11	C24	C23	127.54(16)
C4	C5	C9	107.73(12)	O10	C25	C21	108.68(13)
C6	C5	C9	107.99(13)	O10	C25	C26	107.47(13)
O3	C6	C5	112.37(13)	C21	C25	C26	108.48(13)
O4	C6	O3	120.27(14)	C25	C26	C27	108.29(13)
O4	C6	C5	127.33(15)	C26	C27	C23	107.53(13)
O3	C7	C3	108.22(13)	C26	C27	C32	111.83(13)
O3	C7	C8	107.11(13)	C28	C27	C23	108.91(13)
C3	C7	C8	109.12(13)	C28	C27	C26	111.00(13)
C7	C8	C9	108.97(13)	C28	C27	C32	109.40(14)
C8	C9	C5	106.42(12)	C32	C27	C23	108.05(12)
C10	C9	C5	108.80(13)	O12	C28	C27	114.35(14)
C10	C9	C8	112.42(13)	C29	C28	O12	109.78(15)
C10	C9	C14	109.74(13)	C29	C28	C27	135.82(16)
C14	C9	C5	107.44(12)	C28	C29	C30	106.78(16)

C14	C9	C8	111.80(13)	C31	C30	C29	106.45(17)
O5	C10	C9	115.76(13)	C30	C31	O12	110.60(17)
C11	C10	O5	109.57(14)	C33A	C32	C27	110.37(17)
C11	C10	C9	134.61(15)	C33B	C32	C27	112.3(2)
C10	C11	C12	107.01(16)	C35A	O14A	C36A	115.5(7)
C13	C12	C11	106.37(16)	C34A	C33A	C32	121.8(4)
C12	C13	O5	110.51(16)	C33A	C34A	C35A	125.8(5)
C15	C14	C9	114.45(13)	O13A	C35A	O14A	122.8(8)
C16	C15	C14	124.36(15)	O13A	C35A	C34A	124.6(8)
C15	C16	C17	123.78(15)	O14A	C35A	C34A	112.7(6)
O6	C17	C16	113.05(14)	C35B	O14B	C36B	111.9(14)
O7	C17	O6	122.53(15)	C34B	C33B	C32	118.9(7)
O7	C17	C16	124.39(15)	C33B	C34B	C35B	121.6(7)
C20	O8	C19	114.34(13)	O13B	C35B	O14B	126.6(14)
C24	O10	C25	113.26(12)	O13B	C35B	C34B	124.2(13)
C31	O12	C28	106.39(14)	O14B	C35B	C34B	109.2(10)
O8	C20	C21	111.87(14)				

Crystal Structure of *Endo*-41

Table S23 Crystal data and structure refinement for 0761_Cole.

Identification code	0761_Cole
Empirical formula	$C_{27}H_{29}NO_8$
Formula weight	495.51
Temperature/K	100(2)
Crystal system	monoclinic
Space group	C2
a/Å	26.9187(10)
b/Å	7.6682(3)
c/Å	12.9814(5)
α/°	90
β/°	108.271(3)
γ/°	90
Volume/Å^3	2544.50(17)
Z	4
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	0.096
F(000)	1048.0
Crystal size/mm^3	0.37 × 0.29 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.262 to 61.606
Index ranges	-38 ≤ h ≤ 38, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	44278
Independent reflections	7883 [R_{int} = 0.0341, R_{sigma} = 0.0320]
Data/restraints/parameters	7883/1/330
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0375, wR_2 = 0.0836
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.0876
Largest diff. peak/hole / e Å^{-3}	0.33/-0.18

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

$Goodness\text{-}of\text{-}fit = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S5

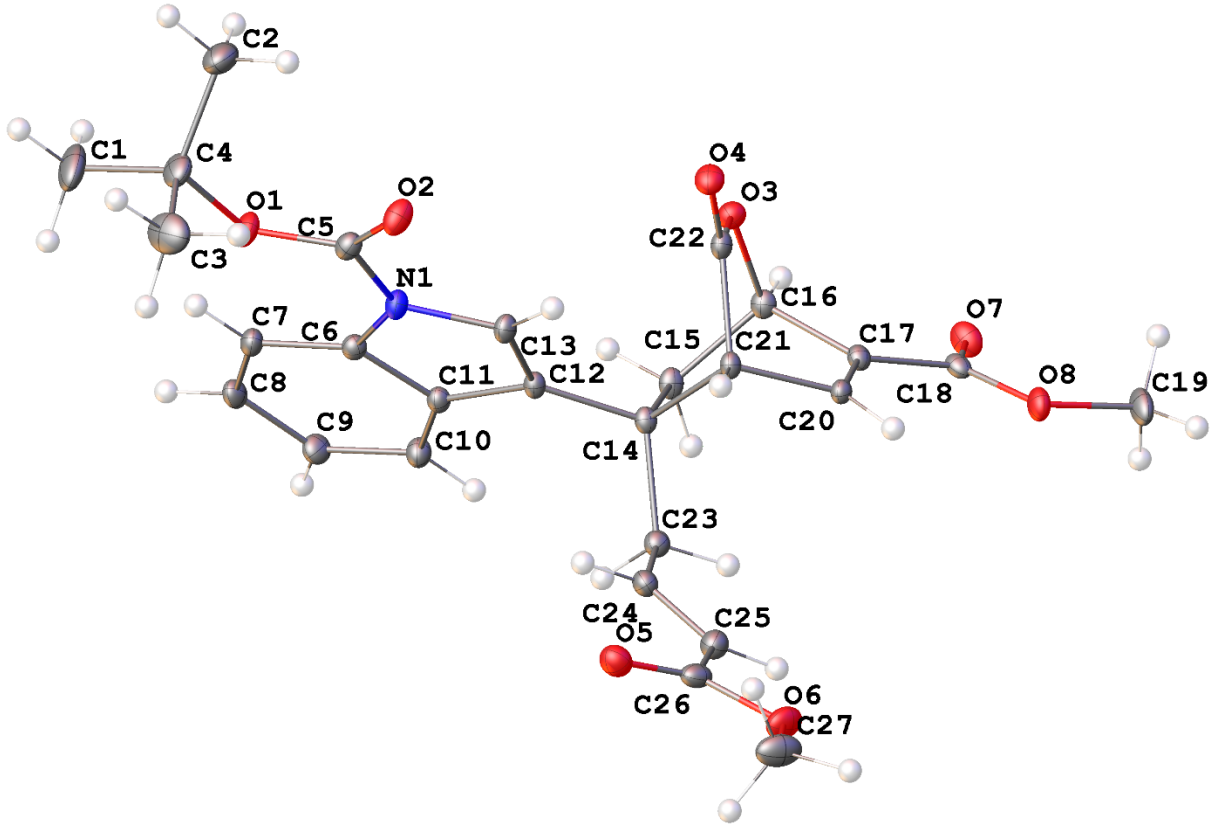


Table S24 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 0761_Cole. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7819.8(5)	1358.3(17)	7163.3(10)	20.4(3)
O2	6979.6(5)	976.9(17)	6097.1(10)	21.2(3)
O3	6123.5(5)	7936.6(16)	5704.6(9)	16.6(2)
O4	5929.2(5)	5342.8(17)	4927.9(9)	19.3(2)
O5	5436.8(5)	620.2(17)	8807.9(10)	23.0(3)
O6	4653.3(5)	1797(2)	8666.3(10)	26.4(3)
O7	5293.3(5)	11844.3(17)	6349.9(10)	22.2(3)
O8	4618.6(5)	9992.0(16)	6112.1(10)	19.6(3)
N1	7196.8(5)	3112.8(19)	7375.7(11)	15.0(3)
C1	8619.5(8)	45(4)	7314.0(19)	40.2(6)
C2	7935.3(8)	164(3)	5489.4(16)	31.2(4)
C3	7814.5(10)	−1817(3)	6943.0(19)	37.3(5)
C4	8039.0(7)	−120(3)	6694.9(15)	24.5(4)
C5	7313.3(6)	1703(2)	6805.6(13)	16.4(3)
C6	7518.8(6)	4117(2)	8230.3(13)	14.1(3)
C7	8056.5(6)	4053(2)	8762.2(13)	16.4(3)
C8	8260.7(6)	5245(2)	9592.7(13)	17.8(3)
C9	7943.2(6)	6449(2)	9893.7(13)	19.3(3)
C10	7409.5(6)	6523(2)	9353.7(13)	17.5(3)
C11	7193.6(6)	5361(2)	8500.5(12)	13.9(3)
C12	6666.6(6)	5121(2)	7759.3(12)	13.1(3)
C13	6687.5(6)	3760(2)	7112.3(13)	14.9(3)
C14	6200.6(6)	6268(2)	7695.8(12)	12.4(3)
C15	6349.7(6)	8229(2)	7648.3(13)	15.2(3)
C16	6021.9(6)	8983(2)	6562.2(13)	14.7(3)
C17	5451.9(6)	8806(2)	6460.0(12)	13.4(3)
C18	5124.5(6)	10381(2)	6313.5(12)	14.9(3)
C19	4265.7(7)	11467(3)	5872.4(15)	25.6(4)
C20	5304.1(6)	7155(2)	6505.6(12)	12.8(3)
C21	5743.2(6)	5870(2)	6617.9(12)	12.6(3)
C22	5939.4(6)	6298(2)	5669.6(13)	14.5(3)
C23	6002.7(6)	5939(2)	8682.6(13)	16.2(3)
C24	5799.2(6)	4133(2)	8711.3(13)	16.9(3)
C25	5333.0(7)	3725(3)	8780.8(14)	20.1(3)
C26	5166.1(7)	1889(3)	8763.3(13)	19.7(4)
C27	4434.2(8)	64(3)	8565.3(17)	32.1(5)

Table S25 Anisotropic Displacement Parameters (Å^2×10^3) for 0761_Cole. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	14.4(5)	21.6(6)	24.7(6)	−5.5(5)	5.4(5)	4.6(5)
O2	15.5(5)	19.3(6)	28.8(6)	−7.9(5)	6.9(5)	−2.0(5)
O3	16.8(6)	15.7(6)	18.1(5)	−0.6(5)	6.7(4)	−1.1(5)

O4	19.9(5)	19.7(6)	17.6(5)	-4.3(5)	4.9(4)	1.1(5)
O5	23.3(6)	23.1(7)	22.1(6)	3.5(5)	6.4(5)	-1.0(5)
O6	17.2(6)	37.3(8)	26.0(6)	-2.0(6)	8.7(5)	-7.8(6)
O7	27.7(7)	13.4(6)	23.0(6)	-0.3(5)	4.3(5)	1.6(5)
O8	17.3(6)	17.7(6)	21.8(6)	0.5(5)	3.1(5)	6.9(5)
N1	11.6(6)	14.0(6)	18.3(6)	-1.3(5)	3.3(5)	1.0(5)
C1	24.3(10)	55.0(15)	37.4(11)	-12.4(11)	4.2(8)	19.7(10)
C2	26.4(9)	44.5(12)	26.0(9)	-2.6(9)	13.1(8)	4.6(9)
C3	53.4(14)	21.8(10)	39.4(11)	1.3(9)	18.7(11)	12.7(10)
C4	23.0(8)	26.8(10)	24.7(9)	-4.1(7)	8.9(7)	9.7(8)
C5	15.9(7)	15.1(7)	19.6(7)	0.4(6)	7.5(6)	0.7(6)
C6	13.2(7)	14.0(7)	15.0(7)	0.7(6)	4.4(6)	-0.5(6)
C7	12.9(7)	18.3(8)	17.9(7)	2.2(6)	4.7(6)	3.2(6)
C8	11.7(7)	23.3(8)	16.3(7)	2.0(7)	1.2(6)	-0.8(6)
C9	15.7(7)	23.9(9)	15.7(7)	-3.0(6)	1.4(6)	-1.4(7)
C10	14.7(7)	19.1(8)	17.4(7)	-1.4(6)	3.1(6)	2.1(6)
C11	11.9(6)	14.6(7)	14.7(7)	1.2(6)	3.2(5)	0.1(6)
C12	10.9(6)	12.2(7)	15.3(7)	0.9(6)	2.6(5)	0.4(6)
C13	10.5(7)	15.0(8)	18.1(7)	-0.5(6)	3.1(6)	-0.3(6)
C14	10.9(6)	10.9(7)	13.7(7)	-1.4(6)	1.2(5)	-0.4(6)
C15	12.3(7)	12.0(7)	19.0(7)	-2.5(6)	1.7(6)	-1.6(6)
C16	14.7(7)	11.2(7)	17.6(7)	-1.0(6)	4.0(6)	-0.6(6)
C17	13.2(7)	13.8(7)	11.6(7)	-1.2(6)	1.6(5)	1.2(6)
C18	19.0(7)	14.4(7)	9.9(6)	-0.6(6)	2.5(5)	2.9(6)
C19	25.6(9)	25.4(10)	22.2(8)	-0.8(7)	2.2(7)	15.4(8)
C20	10.0(7)	15.4(7)	12.4(6)	0.0(6)	2.5(5)	1.0(6)
C21	10.2(6)	11.8(7)	14.3(7)	-0.3(6)	1.7(5)	0.6(5)
C22	10.2(6)	15.4(8)	16.4(7)	-0.2(6)	2.0(5)	1.1(6)
C23	14.7(7)	18.5(8)	14.6(7)	-0.6(6)	3.4(6)	0.5(6)
C24	16.3(7)	19.1(8)	14.6(7)	2.1(6)	3.9(6)	2.8(7)
C25	17.6(8)	23.9(9)	18.9(8)	0.5(7)	5.9(6)	2.0(7)
C26	17.6(8)	29.2(10)	12.6(7)	-0.1(7)	4.9(6)	-4.0(7)
C27	29.3(10)	43.0(13)	26.2(9)	-6.4(9)	11.7(8)	-17.9(9)

Table S26 Bond Lengths for 0761_Cole.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C4	1.492(2)	C7	C8	1.388(2)
O1	C5	1.322(2)	C8	C9	1.394(2)
O2	C5	1.202(2)	C9	C10	1.388(2)
O3	C16	1.4659(19)	C10	C11	1.398(2)
O3	C22	1.346(2)	C11	C12	1.455(2)
O4	C22	1.203(2)	C12	C13	1.352(2)
O5	C26	1.206(2)	C12	C14	1.513(2)
O6	C26	1.348(2)	C14	C15	1.563(2)
O6	C27	1.444(3)	C14	C21	1.577(2)

O7	C18	1.206(2)	C14	C23	1.554(2)
O8	C18	1.337(2)	C15	C16	1.523(2)
O8	C19	1.447(2)	C16	C17	1.504(2)
N1	C5	1.400(2)	C17	C18	1.472(2)
N1	C6	1.405(2)	C17	C20	1.333(2)
N1	C13	1.396(2)	C20	C21	1.511(2)
C1	C4	1.522(3)	C21	C22	1.520(2)
C2	C4	1.517(3)	C23	C24	1.494(2)
C3	C4	1.512(3)	C24	C25	1.324(2)
C6	C7	1.396(2)	C25	C26	1.476(3)
C6	C11	1.411(2)			

Table S27 Bond Angles for 0761_Cole.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	O1	C4	120.31(13)	C12	C14	C15	110.03(12)
C22	O3	C16	112.47(12)	C12	C14	C21	109.84(12)
C26	O6	C27	115.72(16)	C12	C14	C23	110.70(13)
C18	O8	C19	115.29(14)	C15	C14	C21	106.85(12)
C5	N1	C6	130.99(13)	C23	C14	C15	110.31(13)
C13	N1	C5	120.71(13)	C23	C14	C21	109.02(12)
C13	N1	C6	108.29(13)	C16	C15	C14	108.68(13)
O1	C4	C1	101.16(15)	O3	C16	C15	107.66(13)
O1	C4	C2	110.05(16)	O3	C16	C17	108.14(12)
O1	C4	C3	109.37(14)	C17	C16	C15	109.04(13)
C2	C4	C1	111.06(17)	C18	C17	C16	119.34(14)
C3	C4	C1	111.82(19)	C20	C17	C16	113.09(14)
C3	C4	C2	112.76(18)	C20	C17	C18	127.56(15)
O1	C5	N1	110.25(14)	O7	C18	O8	124.28(15)
O2	C5	O1	128.11(16)	O7	C18	C17	123.75(15)
O2	C5	N1	121.63(15)	O8	C18	C17	111.96(14)
N1	C6	C11	106.85(13)	C17	C20	C21	112.85(14)
C7	C6	N1	131.22(15)	C20	C21	C14	109.22(12)
C7	C6	C11	121.92(15)	C20	C21	C22	103.93(12)
C8	C7	C6	117.23(15)	C22	C21	C14	107.69(12)
C7	C8	C9	121.68(14)	O3	C22	C21	113.09(13)
C10	C9	C8	120.90(15)	O4	C22	O3	120.74(15)
C9	C10	C11	118.79(15)	O4	C22	C21	126.15(15)
C6	C11	C12	107.59(14)	C24	C23	C14	113.20(13)
C10	C11	C6	119.43(14)	C25	C24	C23	125.71(16)
C10	C11	C12	132.98(15)	C24	C25	C26	121.00(17)
C11	C12	C14	125.62(14)	O5	C26	O6	123.21(17)
C13	C12	C11	106.67(14)	O5	C26	C25	126.33(16)
C13	C12	C14	127.60(14)	O6	C26	C25	110.44(16)
C12	C13	N1	110.57(14)				

Crystal Structure of *Exo*-41

Table S28 Crystal data and structure refinement for 0737_Cole.

Identification code	0737_Cole
Empirical formula	$C_{27}H_{29}NO_8$
Formula weight	495.51
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.1038(7)
b/Å	12.0566(9)
c/Å	10.4153(7)
α/°	90
β/°	97.827(2)
γ/°	90
Volume/Å^3	1256.95(15)
Z	2
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	0.097
F(000)	524.0
Crystal size/mm^3	0.45 × 0.31 × 0.052
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.196 to 50.172
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-12 \le l \le 12$
Reflections collected	30674
Independent reflections	4414 [R_{int} = 0.0531, R_{sigma} = 0.0377]
Data/restraints/parameters	4414/1/330
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.0848
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.0916
Largest diff. peak/hole / e Å^{-3}	0.17/-0.14

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

Goodness-of-fit = $[\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S6

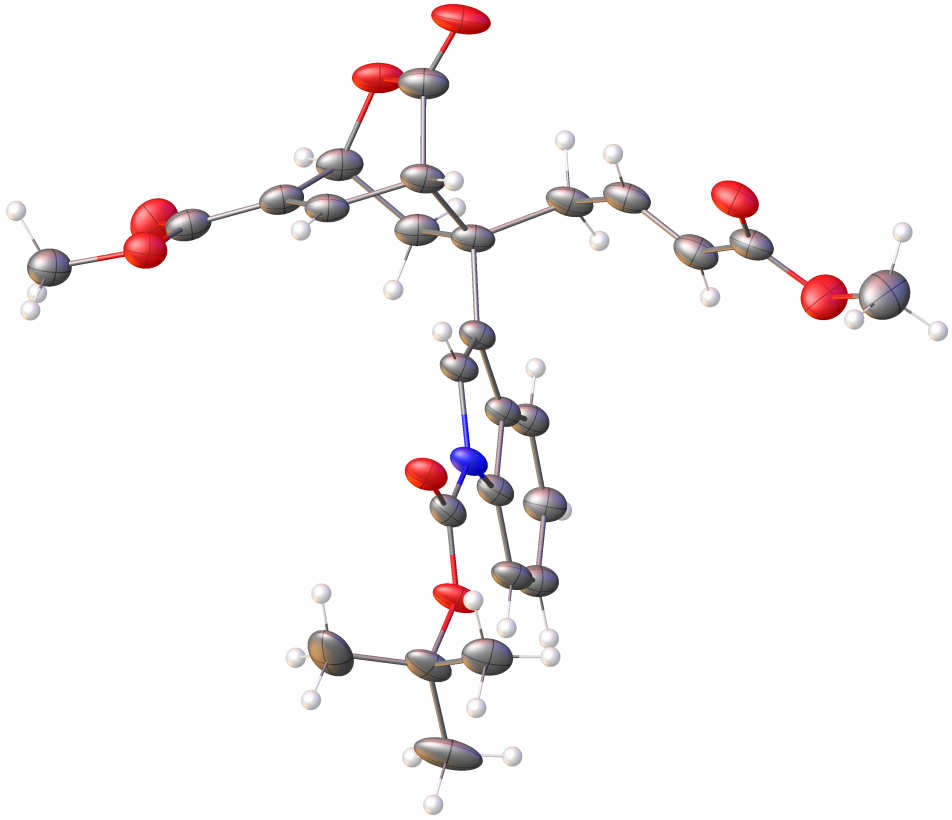


Table S29 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 0737_Cole. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5807(3)	1093(3)	2178(3)	64.7(8)
O2	5832(2)	2743(3)	1198(2)	53.3(7)
O3	1873(3)	5798(3)	1142(3)	65.5(9)
O4	691(2)	6030(3)	2778(2)	53.4(7)
O5	660(2)	7751(3)	6074(3)	64.8(8)
O6	2740(2)	8346(2)	5918(2)	48.8(7)
O7	7578(2)	5218(2)	6325(2)	44.1(7)
O8	7445(2)	4059(2)	8023(2)	45.7(7)
N1	5695(2)	4205(2)	6465(2)	34.6(7)
C1	8710(5)	5597(5)	9115(5)	87.1(18)
C2	8799(4)	3635(5)	9955(4)	80.2(18)
C3	9861(3)	4108(4)	8019(4)	57.0(12)
C4	8749(3)	4393(4)	8779(3)	49.7(11)
C5	6999(3)	4557(3)	6916(3)	37.9(9)
C6	4985(3)	4669(3)	5348(3)	36.8(9)
C7	3732(3)	4260(3)	5146(3)	34.3(8)
C8	3622(3)	3460(3)	6166(3)	35.0(8)
C9	2587(3)	2778(3)	6458(3)	42.1(9)
C10	2776(3)	2134(4)	7555(3)	45.7(10)
C11	3988(3)	2141(4)	8366(4)	45.4(10)
C12	5054(3)	2803(3)	8103(3)	41.7(9)
C13	4853(3)	3455(3)	6998(3)	36.1(8)
C14	6889(5)	745(5)	1511(5)	76.3(15)
C15	5352(4)	2122(4)	1915(4)	46.0(10)
C16	4237(4)	2374(4)	2642(4)	48.2(10)
C17	3514(3)	3283(4)	2417(3)	46.9(10)
C18	2356(3)	3566(4)	3112(3)	45.6(10)
C19	2632(3)	4557(3)	4071(3)	39.5(9)
C20	1315(3)	4847(3)	4625(3)	42.4(9)
C21	872(3)	6011(4)	4198(3)	46.3(10)
C22	1845(4)	5833(4)	2289(4)	53.4(11)
C23	3014(3)	5625(3)	3343(3)	42.5(10)
C24	3101(3)	6594(3)	4249(3)	41.9(9)
C25	1947(3)	6813(3)	4700(4)	43.0(10)
C26	1702(3)	7670(4)	5629(4)	47.1(10)
C27	2539(4)	9297(4)	6730(4)	53.5(11)

Table S30 Anisotropic Displacement Parameters (Å^2×10^3) for 0737_Cole. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	64.0(18)	79(2)	58.5(18)	10.4(17)	33.8(15)	7.5(18)
O2	45.6(15)	79(2)	36.6(14)	1.8(15)	9.6(12)	-14.8(14)
O3	45.7(16)	115(3)	33.1(16)	19.3(16)	-3.1(12)	-10.6(16)

O4	25.8(12)	87(2)	44.6(14)	18.2(14)	-4.5(11)	-2.0(13)
O5	32.8(14)	80(2)	85(2)	6.6(18)	21.8(14)	6.1(14)
O6	33.0(13)	66.5(19)	47.5(15)	4.7(14)	7.6(11)	0.7(13)
O7	25.0(12)	64.7(19)	39.9(14)	-1.4(14)	-5.1(11)	-6.3(12)
O8	20.2(11)	88(2)	27.3(12)	-0.2(13)	-3.7(9)	-7.2(12)
N1	20.3(13)	56(2)	26.0(14)	-3.9(14)	-0.7(11)	-1.3(13)
C1	57(3)	107(5)	84(4)	-42(3)	-38(3)	13(3)
C2	35(2)	160(6)	40(2)	18(3)	-11.3(18)	-22(3)
C3	22.0(17)	94(3)	54(2)	6(2)	1.2(16)	0(2)
C4	19.8(16)	90(3)	36(2)	-9(2)	-7.3(14)	-1.7(18)
C5	21.6(17)	59(2)	33(2)	-8.2(19)	3.0(15)	2.0(17)
C6	24.8(16)	57(3)	28.2(18)	-0.4(17)	2.3(14)	0.1(16)
C7	21.4(16)	52(2)	28.6(17)	-2.6(17)	2.0(13)	0.4(16)
C8	22.6(16)	53(2)	28.8(17)	-3.3(17)	3.0(13)	2.5(16)
C9	26.6(18)	62(3)	37(2)	-1(2)	1.1(15)	-1.0(18)
C10	29.9(18)	66(3)	42(2)	5(2)	7.1(16)	-4.6(18)
C11	33.1(19)	68(3)	36(2)	7(2)	5.0(16)	4.5(19)
C12	25.9(17)	68(3)	29.3(18)	-1.2(19)	-2.9(14)	4.0(17)
C13	22.1(16)	58(2)	28.5(17)	-5.1(18)	4.7(13)	1.0(16)
C14	71(3)	92(4)	74(3)	14(3)	39(3)	11(3)
C15	42(2)	65(3)	30(2)	3(2)	1.1(17)	-13(2)
C16	39(2)	73(3)	33(2)	-1(2)	7.3(16)	-12(2)
C17	32.4(19)	75(3)	31.9(19)	5(2)	-2.0(15)	-16(2)
C18	23.3(17)	79(3)	32.9(19)	3(2)	-3.7(14)	-8.7(18)
C19	19.8(15)	66(3)	31.7(18)	8.8(19)	-0.8(13)	-2.5(16)
C20	19.5(16)	65(3)	42(2)	10.1(19)	1.4(15)	-3.4(17)
C21	20.7(16)	74(3)	44(2)	13(2)	4.8(15)	2.7(18)
C22	33(2)	81(3)	43(2)	16(2)	-3.4(17)	-7(2)
C23	21.0(17)	71(3)	33.9(19)	6.9(19)	-1.1(15)	-2.3(16)
C24	26.6(18)	64(3)	34.3(19)	13(2)	0.1(15)	-1.7(17)
C25	22.0(17)	61(3)	45(2)	16(2)	0.8(16)	4.4(17)
C26	28(2)	64(3)	48(2)	17(2)	4.4(17)	6.2(19)
C27	41(2)	71(3)	50(2)	5(2)	9.1(17)	6(2)

Table S31 Bond Lengths for 0737_Cole.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C14	1.435(5)	C7	C19	1.509(5)
O1	C15	1.339(5)	C8	C9	1.397(5)
O2	C15	1.205(4)	C8	C13	1.415(4)
O3	C22	1.199(5)	C9	C10	1.373(5)
O4	C21	1.465(4)	C10	C11	1.390(5)
O4	C22	1.356(5)	C11	C12	1.397(5)
O5	C26	1.211(4)	C12	C13	1.386(5)
O6	C26	1.330(5)	C15	C16	1.472(5)
O6	C27	1.455(5)	C16	C17	1.321(6)

O7	C5	1.205(4)	C17	C18	1.496(5)
O8	C4	1.496(4)	C18	C19	1.558(6)
O8	C5	1.324(4)	C19	C20	1.561(4)
N1	C5	1.403(4)	C19	C23	1.569(5)
N1	C6	1.397(4)	C20	C21	1.520(6)
N1	C13	1.406(4)	C21	C25	1.494(5)
C1	C4	1.495(7)	C22	C23	1.520(5)
C2	C4	1.523(6)	C23	C24	1.497(5)
C3	C4	1.500(5)	C24	C25	1.341(5)
C6	C7	1.348(4)	C25	C26	1.460(6)
C7	C8	1.450(5)			

Table S32 Bond Angles for 0737_Cole.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C15	O1	C14	115.8(3)	O1	C15	C16	110.6(4)
C22	O4	C21	112.4(3)	O2	C15	O1	123.1(4)
C26	O6	C27	116.5(3)	O2	C15	C16	126.3(4)
C5	O8	C4	120.5(3)	C17	C16	C15	121.6(4)
C5	N1	C13	130.8(3)	C16	C17	C18	123.6(4)
C6	N1	C5	120.7(3)	C17	C18	C19	113.6(3)
C6	N1	C13	108.4(2)	C7	C19	C18	110.1(3)
O8	C4	C2	101.1(3)	C7	C19	C20	111.0(2)
O8	C4	C3	109.3(3)	C7	C19	C23	110.4(3)
C1	C4	O8	109.6(3)	C18	C19	C20	108.7(3)
C1	C4	C2	113.1(4)	C18	C19	C23	110.7(3)
C1	C4	C3	113.1(4)	C20	C19	C23	105.8(3)
C3	C4	C2	110.0(4)	C21	C20	C19	109.3(3)
O7	C5	O8	127.8(3)	O4	C21	C20	107.5(3)
O7	C5	N1	121.9(3)	O4	C21	C25	109.1(3)
O8	C5	N1	110.3(3)	C25	C21	C20	108.9(3)
C7	C6	N1	110.4(3)	O3	C22	O4	121.3(4)
C6	C7	C8	107.0(3)	O3	C22	C23	126.3(4)
C6	C7	C19	127.6(3)	O4	C22	C23	112.4(3)
C8	C7	C19	125.4(3)	C22	C23	C19	105.5(3)
C9	C8	C7	133.3(3)	C24	C23	C19	109.5(3)
C9	C8	C13	119.1(3)	C24	C23	C22	107.4(3)
C13	C8	C7	107.6(3)	C25	C24	C23	113.3(3)
C10	C9	C8	119.4(3)	C24	C25	C21	112.0(4)
C9	C10	C11	120.9(3)	C24	C25	C26	127.3(3)
C10	C11	C12	121.5(3)	C26	C25	C21	120.6(3)
C13	C12	C11	117.2(3)	O5	C26	O6	124.4(4)
N1	C13	C8	106.5(3)	O5	C26	C25	123.0(4)
C12	C13	N1	131.7(3)	O6	C26	C25	112.6(3)
C12	C13	C8	121.9(3)				

Crystal Structure of 46

Table S33 Crystal data and structure refinement for mo_0680_AM_CC04_073_5_0m.

Identification code	mo_0680_AM_CC04_073_5_0m
Empirical formula	$C_{37}H_{32}Br_2O_9$
Formula weight	780.44
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.4799(6)
b/Å	12.7561(5)
c/Å	17.7032(7)
α/°	90
β/°	110.4710(10)
γ/°	90
Volume/Å^3	3275.0(2)
Z	4
ρ_{calc}g/cm^3	1.583
μ/mm^{-1}	2.533
F(000)	1584.0
Crystal size/mm^3	0.34 × 0.28 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.252 to 57.438
Index ranges	$-20 \le h \le 20$, $-16 \le k \le 16$, $-22 \le l \le 23$
Reflections collected	54277
Independent reflections	7686 [R_{int} = 0.0355, R_{sigma} = 0.0334]
Data/restraints/parameters	7686/0/435
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0669
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.0726
Largest diff. peak/hole / e Å^{-3}	0.76/-0.34

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

Goodness-of-fit = $[\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S7

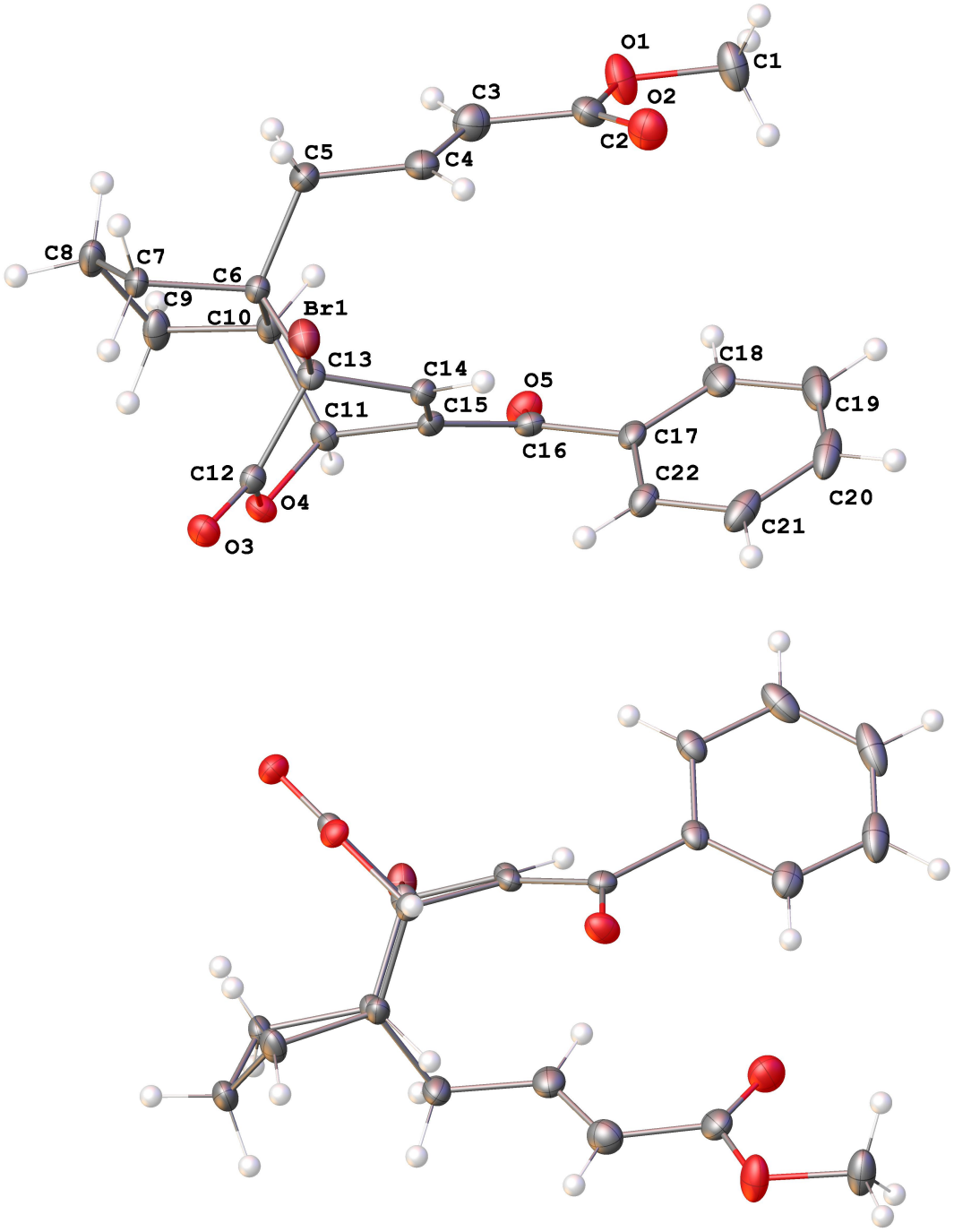

O1
C1
C3
O2
C2
C5
C4
C8
C7
C6
C9
C10
Br1
C13
C14
O5
C18
C19
C11
C15
C16
C17
C12
C22
C20
O4
C21
O3

Table S34 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_0680_AM_CC04_073_5_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	768.6(2)	3993.1(2)	4294.2(2)	25.35(7)
O1	888.5(12)	9517.3(13)	4817.5(9)	36.5(4)
O2	1484.6(12)	8168.6(13)	5635.8(10)	35.1(4)
O3	1220.4(10)	3544.6(11)	2775.2(9)	24.4(3)
O4	1314.1(10)	5168.6(11)	2360.5(8)	20.0(3)
O5	2228.7(10)	8156.4(12)	3217.2(9)	26.6(3)
C1	1501.9(19)	10202.0(19)	5401.6(14)	35.5(6)
C2	956.0(16)	8513.2(19)	5010.6(14)	28.1(5)
C3	288.9(16)	7898.6(19)	4344.8(14)	31.0(5)
C4	296.3(15)	6870.4(19)	4354.6(14)	28.0(5)
C5	-357.1(15)	6194.4(19)	3717.8(14)	26.5(5)
C6	11.1(14)	5643.7(16)	3110.4(12)	19.4(4)
C7	-771.1(14)	4946.3(17)	2552.5(13)	22.0(5)
C8	-1278.9(15)	5661.2(19)	1849.2(14)	29.5(5)
C9	-501.2(15)	6236.8(18)	1686.7(13)	26.1(5)
C10	226.9(14)	6434.8(16)	2528.2(12)	19.9(4)
C11	1221.9(14)	6269.9(16)	2568.7(12)	19.0(4)
C12	1166.6(13)	4467.5(17)	2871.1(12)	18.7(4)
C13	918.6(14)	5016.6(16)	3537.7(12)	18.2(4)
C14	1695.9(13)	5764.3(16)	3936.6(12)	17.8(4)
C15	1852.9(13)	6437.1(16)	3425.1(12)	18.0(4)
C16	2424.4(13)	7394.9(17)	3662.5(12)	19.5(4)
C17	3174.9(14)	7424.9(17)	4463.1(12)	20.5(4)
C18	3355.7(16)	8368.9(19)	4883.6(14)	28.1(5)
C19	4054.3(18)	8424(2)	5631.4(15)	38.3(6)
C20	4584.0(17)	7555(2)	5942.7(14)	39.5(7)
C21	4425.1(16)	6617(2)	5526.5(14)	32.7(6)
C22	3709.0(14)	6545.7(18)	4787.0(13)	23.2(5)
Br2	2476.6(2)	9881.4(2)	1165.0(2)	23.68(7)
O6	3654.0(12)	4405.9(13)	3278.8(9)	34.5(4)
O7	3063.9(10)	4133.4(11)	1942.7(9)	24.4(3)
O8	4679.4(10)	9323.5(11)	3214.2(8)	23.1(3)
O9	4102.6(12)	10793.4(12)	2581.5(10)	35.0(4)
C23	2971.3(17)	3032.9(17)	2087.7(15)	30.8(5)
C24	3412.1(14)	4734.6(17)	2597.3(13)	22.0(5)
C25	3452.3(15)	5841.8(16)	2374.6(13)	21.6(4)
C26	3962.9(14)	6520.0(16)	2920.1(12)	18.5(4)
C27	4044.1(14)	7643.4(16)	2791.2(12)	18.3(4)
C28	3375.8(14)	8147.6(16)	2109.0(12)	19.3(4)
C29	3372.8(14)	9186.8(16)	2025.2(12)	19.6(4)
C30	4039.2(15)	9855.8(17)	2590.1(13)	22.4(5)
C31	4687.1(14)	8261.4(16)	3332.0(12)	18.6(4)
C32	5432.1(14)	7982.0(16)	4089.3(12)	19.2(4)
C33	5669.8(15)	8695.1(17)	4726.9(13)	23.3(5)

C34	6368.1(15)	8471.4(19)	5447.7(13)	26.8(5)
C35	6834.2(15)	7526.7(19)	5545.6(13)	28.2(5)
C36	6606.6(15)	6818.6(19)	4918.0(13)	28.0(5)
C37	5916.9(14)	7039.7(17)	4187.8(13)	23.0(5)

Table S35 Anisotropic Displacement Parameters ($Å^2×10^3$) for mo_0680_AM_CC04_073_5_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	30.54(13)	25.07(12)	20.72(11)	0.70(9)	9.31(9)	−7.44(9)
O1	49.2(11)	30.4(9)	20.9(8)	−3.2(7)	1.1(8)	−6.4(8)
O2	36.8(10)	25.8(9)	39.9(10)	−0.4(8)	9.6(8)	1.8(7)
O3	25.3(8)	19.7(8)	27.5(8)	−3.7(6)	8.3(7)	1.6(6)
O4	23.2(8)	20.5(7)	17.0(7)	−1.7(6)	8.1(6)	2.3(6)
O5	22.6(8)	21.9(8)	32.3(8)	5.4(7)	6.0(7)	1.7(6)
C1	46.7(15)	26.5(13)	25.5(12)	−4.0(10)	3.0(11)	−7.7(11)
C2	27.0(12)	33.4(13)	24.9(12)	−7.2(10)	10.3(10)	2.8(10)
C3	29.7(13)	33.9(14)	27.6(12)	2.1(10)	7.9(10)	2.8(10)
C4	23.3(11)	34.1(13)	29.4(12)	−6.7(10)	12.8(10)	−0.9(10)
C5	18.5(11)	31.9(13)	29.2(12)	−9.9(10)	8.4(9)	−2.3(9)
C6	14.7(10)	21.5(11)	20.6(10)	−5.1(9)	4.4(8)	−1.6(8)
C7	15.5(10)	24.3(11)	23.6(11)	−8.8(9)	3.9(9)	−3.6(8)
C8	20.1(11)	28.6(12)	30.9(12)	−10.0(10)	−2.3(10)	1.7(9)
C9	24.8(11)	22.9(11)	21.1(11)	0.1(9)	−3.7(9)	0.9(9)
C10	18.3(10)	16.5(10)	20.3(10)	−3.8(8)	1.0(9)	1.6(8)
C11	21.5(11)	16.8(10)	18.1(10)	−1.4(8)	6.2(9)	−0.3(8)
C12	15.0(10)	21.2(11)	17.6(10)	−1.3(9)	2.7(8)	0.5(8)
C13	19.0(10)	20.0(11)	15.9(9)	1.5(8)	6.4(8)	−2.5(8)
C14	14.2(10)	21.5(11)	16.4(10)	−2.2(8)	3.5(8)	0.9(8)
C15	12.6(9)	21.2(11)	18.9(10)	−2.7(8)	3.9(8)	2.3(8)
C16	15.3(10)	21.6(11)	23.0(11)	−1.7(9)	8.4(9)	2.1(8)
C17	15.1(10)	27.2(12)	21.1(10)	−2.7(9)	8.6(9)	−5.3(9)
C18	27.1(12)	30.9(13)	31.5(12)	−6.8(10)	16.7(10)	−10.9(10)
C19	38.5(15)	50.4(17)	29.9(13)	−16.5(12)	17.1(12)	−26.5(13)
C20	31.2(13)	66.1(19)	18.5(11)	−1.5(12)	5.5(10)	−26.2(13)
C21	19.2(11)	50.4(16)	25.9(12)	10.5(11)	4.5(10)	−5.6(11)
C22	17.7(11)	31.1(12)	20.4(10)	1.5(9)	6.2(9)	−4.1(9)
Br2	23.47(12)	24.55(12)	19.61(11)	4.33(8)	3.23(9)	5.06(9)
O6	46.1(10)	24.0(9)	25.5(9)	6.0(7)	2.8(8)	−1.8(7)
O7	29.2(8)	17.6(8)	25.4(8)	−0.9(6)	8.5(7)	0.4(6)
O8	26.4(8)	17.8(7)	19.9(7)	2.1(6)	1.8(6)	−0.1(6)
O9	43.6(10)	18.4(9)	30.9(9)	2.8(7)	−2.1(8)	−0.3(7)
C23	38.4(14)	16.5(11)	40.2(13)	−2.1(10)	17.0(11)	0.5(10)
C24	16.9(10)	20.7(11)	26.1(11)	1.8(9)	4.9(9)	3.2(8)
C25	23.0(11)	20.7(11)	20.4(10)	3.4(9)	6.9(9)	1.7(9)
C26	16.6(10)	20.2(11)	19.2(10)	2.6(8)	6.9(8)	2.2(8)

C27	19.3(10)	19.1(10)	17.9(10)	2.1(8)	8.2(8)	1.9(8)
C28	17.9(10)	22.6(11)	18.4(10)	-0.3(9)	7.4(9)	0.2(8)
C29	18.7(10)	22.8(11)	16.7(10)	4.1(8)	5.3(8)	4.3(8)
C30	24.0(11)	21.5(12)	19.1(10)	3.4(9)	4.1(9)	2.8(9)
C31	21.3(11)	16.6(10)	19.8(10)	2.4(8)	9.5(9)	1.9(8)
C32	17.2(10)	22.4(11)	18.9(10)	2.4(9)	7.6(8)	-1.2(8)
C33	22.5(11)	23.0(11)	23.8(11)	0.3(9)	7.5(9)	0.8(9)
C34	25.8(12)	31.8(13)	20.5(11)	-2.9(9)	5.0(9)	-1.6(10)
C35	20.0(11)	39.1(14)	20.8(11)	3.6(10)	1.1(9)	0.2(10)
C36	21.8(11)	29.6(13)	29.2(12)	4.2(10)	4.7(10)	6.4(9)
C37	21.3(11)	24.8(11)	22.3(11)	-0.7(9)	7.0(9)	0.2(9)

Table S36 Bond Lengths for mo_0680_AM_CC04_073_5_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C13	1.942(2)	C17	C22	1.392(3)
O1	C1	1.431(3)	C18	C19	1.388(3)
O1	C2	1.320(3)	C19	C20	1.374(4)
O2	C2	1.206(3)	C20	C21	1.381(4)
O3	C12	1.197(3)	C21	C22	1.391(3)
O4	C11	1.472(2)	Br2	C29	1.884(2)
O4	C12	1.347(2)	O6	C24	1.206(3)
O5	C16	1.221(3)	O7	C23	1.443(3)
C2	C3	1.490(3)	O7	C24	1.336(3)
C3	C4	1.312(3)	O8	C30	1.378(2)
C4	C5	1.497(3)	O8	C31	1.370(2)
C5	C6	1.550(3)	O9	C30	1.201(3)
C6	C7	1.548(3)	C24	C25	1.474(3)
C6	C10	1.560(3)	C25	C26	1.331(3)
C6	C13	1.563(3)	C26	C27	1.463(3)
C7	C8	1.522(3)	C27	C28	1.438(3)
C8	C9	1.521(3)	C27	C31	1.365(3)
C9	C10	1.542(3)	C28	C29	1.334(3)
C10	C11	1.531(3)	C29	C30	1.439(3)
C11	C15	1.504(3)	C31	C32	1.474(3)
C12	C13	1.532(3)	C32	C33	1.395(3)
C13	C14	1.504(3)	C32	C37	1.395(3)
C14	C15	1.330(3)	C33	C34	1.383(3)
C15	C16	1.480(3)	C34	C35	1.384(3)
C16	C17	1.486(3)	C35	C36	1.379(3)
C17	C18	1.392(3)	C36	C37	1.387(3)

Table S37 Bond Angles for mo_0680_AM_CC04_073_5_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	115.64(18)	C15	C16	C17	118.83(18)
C12	O4	C11	114.31(15)	C18	C17	C16	118.4(2)
O1	C2	C3	109.6(2)	C18	C17	C22	119.8(2)
O2	C2	O1	123.9(2)	C22	C17	C16	121.71(19)
O2	C2	C3	126.5(2)	C19	C18	C17	119.9(2)
C4	C3	C2	121.0(2)	C20	C19	C18	119.9(2)
C3	C4	C5	124.4(2)	C19	C20	C21	121.0(2)
C4	C5	C6	117.90(18)	C20	C21	C22	119.6(2)
C5	C6	C10	112.38(17)	C21	C22	C17	119.8(2)
C5	C6	C13	112.49(17)	C24	O7	C23	116.04(17)
C7	C6	C5	107.92(16)	C31	O8	C30	125.10(16)
C7	C6	C10	104.52(16)	O6	C24	O7	123.9(2)
C7	C6	C13	112.63(17)	O6	C24	C25	125.0(2)
C10	C6	C13	106.68(16)	O7	C24	C25	111.10(18)
C8	C7	C6	104.04(17)	C26	C25	C24	119.91(19)
C9	C8	C7	103.15(17)	C25	C26	C27	125.79(19)
C8	C9	C10	104.82(18)	C28	C27	C26	119.54(18)
C9	C10	C6	106.21(16)	C31	C27	C26	122.52(18)
C11	C10	C6	108.94(16)	C31	C27	C28	117.69(19)
C11	C10	C9	113.96(18)	C29	C28	C27	120.76(19)
O4	C11	C10	107.66(16)	C28	C29	Br2	122.02(16)
O4	C11	C15	107.58(16)	C28	C29	C30	122.57(19)
C15	C11	C10	108.41(16)	C30	C29	Br2	115.40(15)
O3	C12	O4	121.45(19)	O8	C30	C29	113.88(18)
O3	C12	C13	127.42(19)	O9	C30	O8	117.53(19)
O4	C12	C13	111.12(17)	O9	C30	C29	128.6(2)
C6	C13	Br1	111.95(13)	O8	C31	C32	109.87(17)
C12	C13	Br1	110.28(14)	C27	C31	O8	119.94(18)
C12	C13	C6	106.63(16)	C27	C31	C32	130.17(19)
C14	C13	Br1	111.82(14)	C33	C32	C31	118.64(19)
C14	C13	C6	109.80(16)	C33	C32	C37	118.84(19)
C14	C13	C12	106.07(16)	C37	C32	C31	122.51(19)
C15	C14	C13	113.34(18)	C34	C33	C32	120.8(2)
C14	C15	C11	112.69(18)	C33	C34	C35	120.0(2)
C14	C15	C16	124.93(19)	C36	C35	C34	119.6(2)
C16	C15	C11	121.07(18)	C35	C36	C37	120.9(2)
O5	C16	C15	119.00(18)	C36	C37	C32	119.8(2)
O5	C16	C17	122.02(19)				

Crystal Structure of 57

Table S38 Crystal data and structure refinement for 0693_Cole.

Identification code	0693_Cole
Empirical formula	$C_{18}H_{16}O_5$
Formula weight	312.31
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.2987(6)
b/Å	10.6941(6)
c/Å	11.9582(7)
α/°	90
β/°	90.7230(10)
γ/°	90
Volume/Å^3	1444.79(14)
Z	4
ρ_{calc}g/cm^3	1.436
μ/mm^{-1}	0.105
F(000)	656.0
Crystal size/mm^3	0.38 × 0.24 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.93 to 57.64
Index ranges	$-15 \le h \le 15$, $-14 \le k \le 14$, $-16 \le l \le 16$
Reflections collected	62679
Independent reflections	7546 [R_{int} = 0.0297, R_{sigma} = 0.0157]
Data/restraints/parameters	7546/1/417
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0772
Final R indexes [all data]	R_1 = 0.0334, wR_2 = 0.0787
Largest diff. peak/hole / e Å^{-3}	0.33/-0.19

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

Goodness-of-fit = $[\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

n: number of independent reflections; p: number of refined parameters

Figure S8

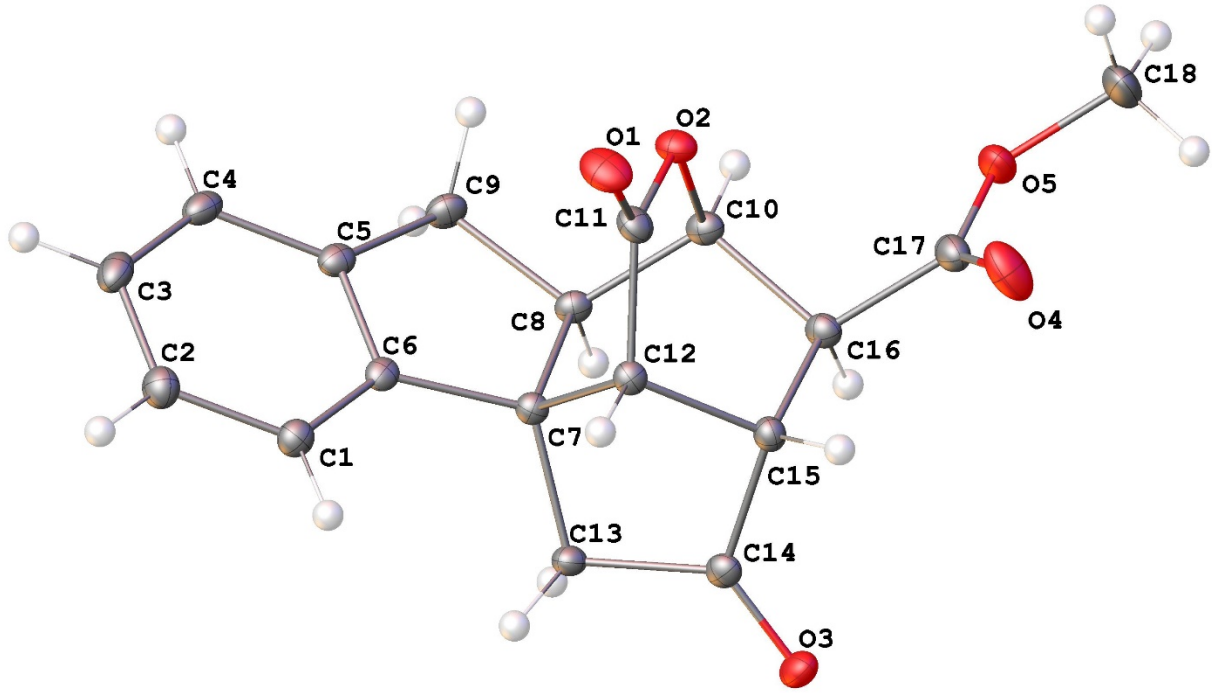


Table S39 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 0693_Cole. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	299.7(12)	7453.9(14)	7845.0(13)	27.2(3)
O2	403.6(11)	5402.6(12)	8118.1(11)	18.3(3)
O3	4785.0(11)	5014.5(13)	6909.2(11)	21.5(3)
O4	1125.1(15)	4795.6(16)	5358.2(13)	34.0(4)
O5	570.4(12)	3061.5(14)	6262.6(11)	25.3(3)
C1	2935.3(15)	7913.6(17)	10260.4(14)	17.1(3)
C2	2568.3(16)	8530.1(18)	11220.3(15)	20.5(3)
C3	1757.7(16)	7963.2(19)	11932.9(15)	21.2(3)
C4	1322.1(15)	6773.9(18)	11706.9(14)	19.4(3)
C5	1703.5(15)	6146.3(16)	10755.0(14)	15.9(3)
C6	2502.3(14)	6720.1(16)	10039.8(13)	14.0(3)
C7	2745.8(14)	5921.6(15)	9032.1(13)	13.0(3)
C8	2065.8(14)	4677.0(16)	9256.9(14)	14.6(3)
C9	1389.1(15)	4843.4(17)	10368.4(15)	18.0(3)
C10	1263.9(15)	4392.2(15)	8252.4(14)	16.1(3)
C11	905.8(15)	6541.4(17)	7951.7(14)	17.3(3)
C12	2232.9(14)	6495.8(15)	7929.1(13)	13.6(3)
C13	4041.1(14)	5691.8(16)	8717.3(14)	14.6(3)
C14	3977.0(15)	5361.1(16)	7481.4(14)	15.5(3)
C15	2704.5(15)	5556.1(16)	7063.0(14)	15.0(3)
C16	1989.1(15)	4323.0(16)	7173.4(14)	16.1(3)

C17	1184.4(16)	4119.0(18)	6155.2(16)	20.3(3)
C18	-209.6(19)	2765(3)	5324.2(18)	34.9(5)
O6	4470.8(11)	3463.9(12)	1063.9(10)	17.8(2)
O7	5119.3(10)	3246.4(11)	2811.3(10)	14.4(2)
O8	3059.4(11)	7035.9(12)	4549.1(10)	19.3(3)
O9	3007.2(12)	2410.4(12)	5048.3(11)	20.6(3)
O10	2684.2(11)	2727.3(12)	3215.5(10)	19.8(3)
C19	6218.2(15)	6627.7(16)	946.1(14)	14.9(3)
C20	7203.4(16)	6587.9(17)	259.8(14)	18.0(3)
C21	8227.8(16)	5976.1(17)	608.4(16)	20.2(3)
C22	8290.1(15)	5384.9(17)	1641.0(16)	19.3(3)
C23	7307.0(14)	5422.7(15)	2333.1(14)	14.9(3)
C24	6281.4(14)	6041.1(15)	1981.5(13)	12.9(3)
C25	5301.7(14)	5902.3(15)	2810.2(13)	11.7(3)
C26	5858.9(14)	5092.4(15)	3776.1(13)	12.3(3)
C27	7170.8(14)	4858.2(16)	3477.1(13)	15.0(3)
C28	5133.5(14)	3900.5(15)	3886.9(13)	13.1(3)
C29	4571.5(14)	3901.6(15)	1987.0(13)	13.3(3)
C30	4205.7(13)	5188.0(15)	2331.6(13)	11.6(3)
C31	4707.4(14)	7082.3(15)	3257.0(14)	14.1(3)
C32	3624.7(14)	6545.7(16)	3825.7(13)	13.8(3)
C33	3390.7(14)	5219.4(15)	3358.7(13)	12.6(3)
C34	3844.8(14)	4227.0(15)	4198.4(13)	13.1(3)
C35	3122.8(14)	3034.8(15)	4220.2(14)	14.8(3)
C36	2203.9(17)	1475.0(18)	3129.6(17)	23.9(4)

Table S40 Anisotropic Displacement Parameters ($Å^2×10^3$) for 0693_Cole. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	20.9(6)	21.6(7)	39.0(8)	0.1(6)	-7.6(6)	6.1(5)
O2	13.3(5)	17.9(6)	23.5(6)	0.1(5)	-0.6(5)	0.7(5)
O3	18.5(6)	22.5(6)	23.7(6)	-6.7(5)	5.7(5)	-0.9(5)
O4	41.5(9)	29.7(8)	30.5(8)	3.0(6)	-16.4(6)	-6.7(7)
O5	22.0(6)	30.3(7)	23.6(6)	-7.7(6)	2.0(5)	-11.0(6)
C1	18.5(8)	16.9(7)	16.1(7)	1.6(6)	0.7(6)	0.5(6)
C2	22.5(8)	19.0(8)	19.9(8)	-2.1(7)	-0.6(6)	1.2(7)
C3	19.4(8)	27.1(9)	17.2(8)	-2.8(7)	0.7(6)	7.1(7)
C4	14.3(7)	27.6(9)	16.2(7)	2.5(7)	2.2(6)	3.7(7)
C5	13.4(7)	18.9(8)	15.3(7)	2.8(6)	-0.5(6)	2.7(6)
C6	13.3(7)	15.7(7)	12.9(7)	2.0(6)	-1.5(5)	3.5(6)
C7	13.6(7)	11.6(7)	13.8(7)	1.2(6)	0.0(5)	-0.3(6)
C8	14.4(7)	12.9(7)	16.4(7)	2.6(6)	1.5(6)	-0.3(6)
C9	17.1(7)	18.7(8)	18.4(8)	3.8(6)	4.0(6)	-0.9(6)
C10	15.4(7)	13.1(7)	19.8(8)	0.1(6)	1.4(6)	-0.6(6)
C11	16.2(7)	18.1(8)	17.5(7)	-0.3(6)	-3.8(6)	0.6(6)

C12	15.1(7)	11.8(7)	14.0(7)	1.7(6)	-0.3(5)	0.0(6)
C13	11.7(7)	16.6(7)	15.5(7)	0.3(6)	0.2(6)	-0.4(6)
C14	16.1(7)	12.2(7)	18.4(8)	-0.6(6)	1.6(6)	-2.7(6)
C15	16.0(7)	14.7(7)	14.4(7)	-1.0(6)	-0.2(6)	-1.1(6)
C16	15.8(7)	13.9(7)	18.7(7)	-0.9(6)	0.2(6)	-1.5(6)
C17	17.4(8)	21.1(8)	22.3(8)	-6.7(7)	-1.0(6)	-0.7(7)
C18	26.7(10)	49.2(13)	28.7(10)	-15.3(10)	0.5(8)	-16.8(10)
O6	19.5(6)	18.8(6)	15.1(5)	-4.7(5)	-0.6(4)	-0.1(5)
O7	15.8(5)	12.5(5)	14.8(5)	-2.0(4)	-1.4(4)	1.4(4)
O8	20.3(6)	17.9(6)	19.9(6)	-3.1(5)	3.3(5)	2.5(5)
O9	21.5(6)	18.1(6)	22.2(6)	7.1(5)	0.6(5)	-1.4(5)
O10	21.7(6)	19.1(6)	18.6(6)	-1.1(5)	-1.8(5)	-6.1(5)
C19	15.7(7)	12.4(7)	16.7(7)	0.2(6)	0.2(6)	-0.3(6)
C20	20.4(8)	15.5(7)	18.0(7)	1.1(6)	4.3(6)	-0.9(6)
C21	17.0(8)	19.4(8)	24.3(8)	-0.9(7)	7.0(6)	-0.6(7)
C22	13.6(7)	18.7(8)	25.7(8)	0.0(7)	0.4(6)	1.2(6)
C23	14.5(7)	12.5(7)	17.6(7)	-1.4(6)	-1.7(6)	-1.5(6)
C24	13.4(7)	11.1(7)	14.0(7)	-1.1(6)	1.1(5)	-1.3(6)
C25	12.1(7)	10.9(7)	12.2(6)	-1.1(5)	-1.2(5)	-0.3(6)
C26	13.1(7)	12.5(7)	11.3(6)	-0.2(6)	-1.4(5)	0.0(6)
C27	12.8(7)	16.3(7)	15.8(7)	0.5(6)	-2.2(6)	1.1(6)
C28	14.6(7)	12.4(7)	12.1(7)	0.4(6)	-1.9(5)	0.7(6)
C29	10.9(7)	13.0(7)	16.1(7)	-0.2(6)	0.4(5)	-1.6(6)
C30	11.2(6)	12.2(7)	11.3(6)	-0.5(5)	-1.5(5)	0.0(5)
C31	14.3(7)	11.9(7)	16.2(7)	-1.2(6)	1.7(6)	0.2(6)
C32	14.5(7)	12.7(7)	14.3(7)	0.7(6)	-1.3(5)	1.9(6)
C33	12.5(7)	11.3(7)	13.9(7)	0.1(6)	0.3(5)	0.4(5)
C34	15.1(7)	12.3(7)	12.0(7)	1.2(5)	0.3(5)	0.3(6)
C35	12.1(7)	14.1(7)	18.1(7)	0.5(6)	1.2(6)	1.3(6)
C36	21.7(8)	18.9(8)	31.1(9)	-5.4(7)	-1.7(7)	-6.1(7)

Table S41 Bond Lengths for 0693_Cole.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C11	1.198(2)	O6	C29	1.203(2)
O2	C10	1.461(2)	O7	C28	1.4640(19)
O2	C11	1.359(2)	O7	C29	1.353(2)
O3	C14	1.206(2)	O8	C32	1.202(2)
O4	C17	1.198(3)	O9	C35	1.203(2)
O5	C17	1.334(2)	O10	C35	1.335(2)
O5	C18	1.453(2)	O10	C36	1.448(2)
C1	C2	1.391(2)	C19	C20	1.392(2)
C1	C6	1.391(2)	C19	C24	1.389(2)
C2	C3	1.397(3)	C20	C21	1.389(3)
C3	C4	1.389(3)	C21	C22	1.388(3)
C4	C5	1.394(2)	C22	C23	1.394(2)

C5	C6	1.394(2)	C23	C24	1.395(2)
C5	C9	1.509(2)	C23	C27	1.505(2)
C6	C7	1.505(2)	C24	C25	1.502(2)
C7	C8	1.562(2)	C25	C26	1.569(2)
C7	C12	1.560(2)	C25	C30	1.558(2)
C7	C13	1.536(2)	C25	C31	1.529(2)
C8	C9	1.552(2)	C26	C27	1.550(2)
C8	C10	1.526(2)	C26	C28	1.522(2)
C10	C16	1.539(2)	C28	C34	1.547(2)
C11	C12	1.501(2)	C29	C30	1.496(2)
C12	C15	1.543(2)	C30	C33	1.545(2)
C13	C14	1.520(2)	C31	C32	1.520(2)
C14	C15	1.531(2)	C32	C33	1.546(2)
C15	C16	1.553(2)	C33	C34	1.544(2)
C16	C17	1.526(2)	C34	C35	1.514(2)

Table S42 Bond Angles for 0693_Cole.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O2	C10	113.60(13)	C29	O7	C28	113.11(12)
C17	O5	C18	114.95(17)	C35	O10	C36	115.22(14)
C6	C1	C2	118.91(16)	C24	C19	C20	118.64(16)
C1	C2	C3	120.13(17)	C21	C20	C19	120.47(16)
C4	C3	C2	120.79(17)	C22	C21	C20	120.94(16)
C3	C4	C5	119.16(16)	C21	C22	C23	118.89(16)
C4	C5	C9	128.36(16)	C22	C23	C24	120.00(15)
C6	C5	C4	119.89(16)	C22	C23	C27	128.27(15)
C6	C5	C9	111.74(15)	C24	C23	C27	111.73(14)
C1	C6	C5	121.10(16)	C19	C24	C23	121.08(15)
C1	C6	C7	127.23(15)	C19	C24	C25	127.06(14)
C5	C6	C7	111.58(15)	C23	C24	C25	111.75(14)
C6	C7	C8	104.50(13)	C24	C25	C26	104.36(12)
C6	C7	C12	112.58(13)	C24	C25	C30	113.26(12)
C6	C7	C13	118.13(13)	C24	C25	C31	118.65(13)
C12	C7	C8	107.62(13)	C30	C25	C26	108.03(13)
C13	C7	C8	112.22(13)	C31	C25	C26	111.85(13)
C13	C7	C12	101.58(12)	C31	C25	C30	100.52(12)
C9	C8	C7	107.36(13)	C27	C26	C25	107.18(12)
C10	C8	C7	108.85(13)	C28	C26	C25	108.35(12)
C10	C8	C9	113.77(14)	C28	C26	C27	113.73(13)
C5	C9	C8	104.57(13)	C23	C27	C26	104.71(13)
O2	C10	C8	109.05(13)	O7	C28	C26	108.88(12)
O2	C10	C16	107.70(13)	O7	C28	C34	108.62(12)
C8	C10	C16	110.64(14)	C26	C28	C34	109.96(13)
O1	C11	O2	120.42(16)	O6	C29	O7	120.27(15)
O1	C11	C12	126.47(17)	O6	C29	C30	125.97(15)

O2	C11	C12	113.11(14)	O7	C29	C30	113.65(13)
C11	C12	C7	110.98(13)	C29	C30	C25	109.33(13)
C11	C12	C15	112.76(13)	C29	C30	C33	114.12(13)
C15	C12	C7	100.57(12)	C33	C30	C25	100.15(12)
C14	C13	C7	103.99(13)	C32	C31	C25	101.79(13)
O3	C14	C13	126.57(16)	O8	C32	C31	126.54(16)
O3	C14	C15	124.82(16)	O8	C32	C33	124.76(15)
C13	C14	C15	108.61(13)	C31	C32	C33	108.65(13)
C12	C15	C16	108.14(13)	C30	C33	C32	101.90(12)
C14	C15	C12	101.55(13)	C34	C33	C30	107.79(12)
C14	C15	C16	110.14(14)	C34	C33	C32	109.99(12)
C10	C16	C15	108.28(13)	C33	C34	C28	107.73(12)
C17	C16	C10	110.96(14)	C35	C34	C28	108.85(13)
C17	C16	C15	111.04(14)	C35	C34	C33	114.53(13)
O4	C17	O5	124.39(17)	O9	C35	O10	124.14(16)
O4	C17	C16	125.12(17)	O9	C35	C34	123.08(15)
O5	C17	C16	110.47(16)	O10	C35	C34	112.70(14)